SYNTHESIS OF NOVEL CARBON NANOTUBE MEMBRANES FOR APPLICATIONS IN WATER TREATMENT

BY

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Dedicated to my beloved parents, fiance, teachers, brothers, sisters and friends

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ABSTRACT

Full Name : **IHSANULLAH**

Thesis Title : **SYNTHESIS OF NOVEL CARBON NANOTUBE MEMBRANES FOR APPLICATIONS IN WATER TREATMENT**

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Carbon nanotubes (CNTs) are considered to be a versatile and unique material due to their extraordinary electrical, thermal and mechanical properties. CNTs have been extensively utilized for the removal of various contaminants from water. In this work, a novel approach was used to synthesize metal/metal oxide doped-CNT membranes, with the aim of fully utilizing the extra ordinary properties of CNTs and metal/metal oxides. No binder was used for the synthesis of the membrane; instead, metal/metal oxide particles served as a binding material for the CNTs during sintering at high temperature. In the first step, CNTs were impregnated with different loadings of metal/metal oxide (1, 10 and 20 wt%) via a wet chemistry technique. Iron oxide, aluminum oxide and silver nanoparticles were impregnated on the surface of CNTs. Impregnated CNTs were then compacted at high pressure and sintered at high temperature to form a compact disc (membrane). The powder materials were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and thermogravimetric analysis; while the membranes were characterized by measuring their porosity, contact angle, diametrical compression test and pure water permeate flux. The membranes were used for the removal of selected heavy metals from water in a continuous filtration system. The effect of solution pH, initial concentration, time and metal oxide loading were

studied on the removal of heavy metal from water. The permeate flux and rejection rate of sodium alginate (SA) were determined to predict the antifouling behavior of the membrane. The affinity of the membranes to biofouling was studied using *Escherichia coli* (E. coli). The produced membranes showed a high water permeate flux and exhibited a strong antibacterial property. These membranes showed excellent potential for the removal of heavy metals from water and exhibited strong antifouling behavior.

الملخص الرسالة

الاسم الكامل: احسان الله

عنوان الرسالة: اصطناع مبتكر لأغشية الأنابيب النانوية الكربونية للتطبيقات في معالجة المياه

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: : ديسمبر 2015

تعتبر أنابيب الكربون النانوية (CNTs) مادة متعددة الاستعمالات وفريدة من نوعها بسبب الخواص الكهربائية والحرارية والميكانيكية استثنائية الخاصة بهم. في هذه الدراسه قد تم استخدام الأنابيب النانوية الكربونية (CNTs) على نطاق واسع لإزالة مختلف الملوثات من المياه.وكان يستخدم نهجا جديدا لتجميع المعادن / اكسدة سطح المعدن – للانابيب النانويه الكربونيه للاغشية ، بهدف الاستفادة الكاملة من الخصائص الغير مالوفه من الأنابيب النانوية الكربونية وأكاسيد المعادن / اكاسيد المعادن. ولم يستخدم الترابط لتركيب الغشاء. بدلا من ، المعادن/ شكلت جزيئات أكسيد المعادن كمادة ملزمة لتشارك للانابيب النانويه الكربونيه للاغشية خلال التكلس في درجة حرارة عالية. في الخطوة الأولى، كانت الأنابيب النانوية الكربونية (CNTs) المخصبة بنسب مختلفة من المعادن / اكاسيد المعادن (1 و 10 و 20٪ بالوزن) عبر تقنية الكيمياء الرطبة. شكلت أكسيد الحديد المخصبه، وأكسيد الألمنيوم والفضة النانوية على سطح الأنابيب النانوية الكربونية. وبعد ذلك ضغط الأنابيب النانوية الكربونية CNTs) المشبعة في ارتفاع الضغط والمتكلسه في درجة الحرارة العالية لتشكيل القرص المضغوط (غشاء). تميزت مسحوق المواد من قبل المجهر الإلكتروني، انتشار للطاقة الأشعة السينية التحليل الطيفي، حيود الأشعة السينية والتحليل الوزني الحراري. في حين تميزت الأغشية عن طريق قياس المسامية، وزاوية التماس، واختبار الضغط القطري ونقية تدفق تتخلل المياه. تم استخدام الأغشية لإزالة المعادن الثقيلة المختارة من المياه في نظام الترشيح المستمر. تم دراسة تأثير الرقم الهايدروجينى (pH)، والتركيز الأول, تمت دراسة الوقت وأكسيد معدن يوضع لإزالة المعادن الثقيلة من المياه. تم تحديد معدل تدفق ورفض (Sodium Alginate) لحمايه الغشاء من الترسبات. وقد تمت دراسه الترسبات الحيويه على الاغشيه بواسطه (E.coli). وأظهرت الأغشية إنتاج عالية التدفق تتخلل المياه وأظهرت خاصية قويه مضاد للجراثيم. وأظهرت هذه الأغشية إمكانيات ممتازة لإزالة المعادن الثقيلة من المياه وأظهرت سلوك قوى لمن الترسبات.

CHAPTER 1

INTRODUCTION

Water is the life blood of the modern era as a result of the scarcity of resources, lack of rain and increase in the space of desert on green space. As per a report from the United Nations (UN), by 2025, 1800 million people will be facing absolute water scarcity, and two-thirds of the world population could be under stress conditions [1, 2]. Water reuse/recycle/ recovery have proven to be successful and effective in creating an alternate water supply.

1.1 Applications of Membranes in Water Treatment

Membrane filtration is considered among the most promising and widely used processes for water treatment and desalination [1, 2]. Membranes are classified into different types based on their nominal size or molecular weight cut-off (MWCO) including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Microfiltration is employed for bacteria, protozoa and suspended solids removal, ultrafiltration for colloid and virus removal, nanofiltration for heavy metals, dissolved organic matter and hardness removal and reverse osmosis for ultrapure water production, water reuse and desalination [3].

Membranes can also be classified based on their configurations including hollow fiber, spiral, plate-and-frame and tubular. Membranes are manufactured from ceramic,

polymeric, or hybrid materials. The most common polymeric membranes are poly(sulfone), poly(amide), poly(propylene), poly(tetrafluoroethylene), cellulose acetate, and poly(vinylidene) fluoride. Most of the ceramic membranes are made of metal oxides including aluminium oxide (Al_2O_3); titanium oxide (TiO_2); silica (SiO_2); zeolites; microporous carbon; silicon carbide (SiC) and zirconia (ZrO_2). Ceramic membranes are well suited for challenging water purification process due to their chemical and thermal stabilities. However, ceramic membranes are typically considered too expensive and are recommended only for small scale operations. Polymeric membranes, on the other hand, are dominating the current water desalination and purification market because of their excellent mechanical strength under pressure and high selectivity. However, in many wastewater applications, the current polymeric membranes are chemically unstable and less fouling-resistant than ceramic membranes [4].

1.2 Carbon Nanotubes in Water Treatment

Carbon nanotubes (CNTs) have been widely explored by scientists in several fields e.g. chemistry, physics and materials science owing to their unique properties such as high aspect ratio, low density, high chemical, thermal, and mechanical strength and remarkable electrical and optical properties. CNTs have been employed for the removal of various contaminants from aqueous solutions. Various experimental studies have reported the adsorption of heavy metal ions [6-13], small molecules like hydrogen and oxygen [14-15] and organic chemicals [17-19] on different CNTs (closed- or open-ended CNTs, single walled or multiwalled).

1.3 Carbon Nanotube Membranes

CNTs have recently attracted considerable attention for the synthesis of novel membranes with attractive features for water purification [20-36]. CNTs can also be used as direct filters and effective fillers to improve the membrane performance. CNTs have proven to be excellent filler in membrane due to improved antifouling behavior, disinfection, rejection and permeability. The flux of certain molecules through CNTs, as estimated by molecular dynamics simulation have been found to be 3-4 orders of magnitude higher than predicted by the Hagen-Poiseuille equation [22-24].

In the literature, different approaches have been reported by researchers for the synthesis of CNT based membranes:

1. Template-prepared carbon nanotube membranes, in which carbonaceous materials are deposited inside pre-existing ordered porous membranes, e.g anodized alumina [27-28, 37].
2. Aligned-array outer-wall CNT membranes in which the interstices between vertical array of CNTs serves as membrane [29, 37].
3. Composite membranes of aligned CNT/polymer or aligned CNT/ceramic [24, 26, 37].
4. Buckypaper membranes [37-38].
5. Multistacked membranes composed of bundles of vertically aligned CNTs [37].
6. Mixed-matrix membranes, where CNTs are used as fillers in a polymer matrix [39-44].

Recently, the mixed-matrix membrane has been explored extensively due to ease of synthesis and broad applications. Different nanoparticles such as TiO_2 [45-46], Al_2O_3 [47–48], ZrO_2 [49], SiO_2 [50] have been used as a filler materials for the synthesis of mixed-matrix membranes with improved performance. Several studies have shown successful application of CNTs in polymer matrix [39-44]. Addition of CNTs has been reported to substantially increase the water flux due to hydrophilic surface and large surface pores of the membranes [40]. Moreover, the tensile strength and fouling resistance of the membranes were reported to increase with addition of CNTs. Several studies have been performed, in recent years, with the goal to enhance the fouling resistance of membrane by surface modification with CNTs [5, 51].

1.4 Significance of the Study

The present work describes a novel approach to synthesize carbon nanotube membranes, comprised of CNTs and metal/metal oxide nanoparticles. CNTs impregnated with iron oxide, aluminum oxide and silver nanoparticles were used for the synthesis of the membranes. These CNTs based membranes were effective in removing a number of contaminants from water. They exhibited the potential advantage of coupling the adsorptive properties of CNTs and sieving properties of membrane structure. CNT-based membranes can be effectively employed in continuous filtration system for the removal of heavy metals from water. Furthermore, the antifouling behavior of these membranes made them suitable to treat water containing inorganic and organic foulants. The CNT-Fe_2O_3 membranes showed excellent antifouling potential for sodium alginate removal, and CNT-Ag membranes were able to completely remove E-coli bacteria in a short time

from water. These membranes also showed excellent removal efficiency for heavy metals from water.

1.5 Objectives of the Study

The aim of the proposed work is to synthesize novel carbon nanotube membranes that are capable of efficiently removing different contaminants from water. The specific objectives are:

1. To impregnate surface of the carbon nanotubes (CNTs) with different metal and metal oxides.

2. To characterize the prepared materials by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

3. To design and fabricate an advanced carbon filtration system.

4. To remove the different contaminants from water using the developed advanced carbon filtration system.

5. To optimize the removal parameters in the water filtration system.

1.6 Thesis Summary

This section highlights the summary of each chapter in the thesis.

Chapter 1

Chapter 1 induces the introduction section of the thesis. It provides a brief summary of the carbon nanotubes applications in water treatment. The available techniques for the synthesis of carbon nanotube membrane are discussed briefly. It also highlights the

objectives and significance of the study. The summary of all the chapters is presented at the end of chapter 1.

Chapter 2

Chapter 2 presents a comprehensive review on the use of carbon nanotubes (CNTs) for the adsorptive removal of the heavy metals (lead, chromium, cadmium, arsenic, copper, zinc and nickel). A review of the effect of a number of key variables including pH, CNTs dosage, time, ionic strength, temperature and surface charge is given. It is demonstrated that surface modification (using acid treatment) enhances positively the adsorption capacity of CNTs towards cadmium, chromium, lead, mercury, copper, zinc and nickel as did the solution pH. CNTs have been proven to be an excellent adsorbent for the removal of different heavy metals from water. However, most of the applications of CNTs are on lab scale in batch experiments. In spite of high costs, CNTs are expected to be a promising adsorbent in the future due to their high adsorption capacity compared to many traditional adsorbents. Effective techniques for regeneration/reuse of CNTs also need to be explored yet. One of the main hurdles that limit the applications of CNTs in large scale operation is the cost of CNTs. Future research work is recommended for the effective analysis of the toxicity of CNTs and developing an economical way for the production of CNTs.

Chapter 3

Chapter 3 provides a comprehensive overview of the different CNT membranes that have been reported by researchers so far. Different approaches for the synthesis of CNT membranes and the interaction between the CNTs is discussed. The last portion of the

chapter is focused on the mixed matrix membranes. The effect of different fillers on the membrane properties is also presented.

Chapter 4

Chapter 4 presents a novel approach to synthesize an iron oxide doped carbon nanotube (CNT) membrane, with the goal of fully utilizing the unique properties of CNTs. No binder was used for the synthesis of the membrane; instead, iron oxide particles served as a binding agent for holding the CNTs together after sintering at high temperature. The produced membrane exhibited a high water flux and strong fouling resistance. In the first step, CNTs were impregnated with various loadings of iron oxide (1, 10, 20, 30 and 50%) via wet chemistry techniques. Impregnated CNTs were then compacted at 200 MPa and sintered at 1350 °C for 5 h to form a compact disc. The membranes were analysed by measuring their porosity, contact angle, diametrical compression test and water flux. The flux of pure water was observed to increase with an increase in iron oxide content. The permeate flux and rejection rate of sodium alginate (SA) were determined to predict the antifouling behaviour of the membrane. A maximum removal of 90 and 88% of SA was achieved for membranes with a 10 and 1% iron oxide content, respectively, after 3 h. A minor decline in the permeate flux was observed for all membranes after 4 h of operation.

Chapter 5

Chapter 5 presents the synthesis and application of silver doped-CNT membrane. A novel approach was used to synthesize a silver doped-CNT membrane, with the aim of fully utilizing the antitoxic properties of CNTs and silver. No binder was used for the synthesis of the membrane; instead, silver particles served as a binding material for the CNTs after sintering at high temperature. In the first step, CNTs were impregnated with different

loadings of silver (1, 10 and 20 wt.%) via a wet chemistry technique. Impregnated CNTs were then compacted at 200 MPa and sintered at 800 °C for 3 h to form a compact disc (membrane). The powder materials were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and thermogravimetric analysis; while the membranes were characterized by measuring their porosity, contact angle, diametrical compression test, pure water permeate flux and antibacterial properties. The affinity of the membranes to biofouling was studied using Escherichia coli (E. coli). The produced membrane showed a high water permeate flux and exhibited strong antibacterial properties. All of the membranes with different silver loadings were able to remove/kill 100% of the bacteria tested; however, the CNT membrane with 10% silver showed a superior performance to the others. All bacteria were removed/killed by the membrane with 10% silver loading after the suspension had passed for only 60 min. These membranes would be advantageous in a continuous filtration system for the removal of different contaminants from water via desalination, adsorption and sieving.

Chapter 6

Chapter 6 describes the applications of carbon nanotube membranes for the removal of hexavalent chromium from water in the continuous filtration system. Metal-oxide doped-carbon nanotube membranes were synthesized using a novel approach and employed for the removal of hexavalent chromium from aqueous solution. The removal was affected by the metal oxide loading, initial solution concentration, pH and time. Maximum removal of 92% of Cr(VI) was observed at pH 6 and initial concentration of 0.5 ppm by membrane with 10% Fe_2O_3 loading after 3 hours of operation. Membrane with 10% Al_2O_3 was able to remove 79% of Cr(VI) ions under similar experimental conditions.

These results suggest that the CNT- metal oxide membrane can be employed effectively in continuous filtration system for the removal of Cr(VI) ions.

Chapter 7

Chapter 7 presents a brief summary of the outcome of this study. Recommendations for the future work are also included in this chapter.

References

[1] X. Qu, P.J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res. 47 (2013) 3931–3946.

[2] S. Kar, R.C. Bindal, P.K. Tewari, Carbon nanotube membranes for desalination and water purification: Challenges and opportunities, Nano Today 7 (2012) 385-389.

[3] M. Cheryan. Ultrafiltration and Microfiltration Handbook. 2nd ed. CRC Press, 1998.

[4] M.M. Pendergast, E.M.V. Hoek. A review of water treatment membrane nano-technologies, Energy Environ. Sci. 4 (2011) 1946-1971.

[5] R. Mallada, M. Menéndez, Inorganic membranes: synthesis, characterization and applications, 1st ed. Oxford: Elsevier, 2008.

[6] Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes, Carbon 4 (2003) 2787–2792.

[7] Ihsanullah, F. A. A. Khaldi, B. Abusharkh, M. Khaled, M.A. Atieh, M.S. Nasser, T. laoui, S. Agarwal, I. Tyagi, V. K. Gupta, Adsorptive removal of Cadmium (II) ions from liquid phase using acid modified carbon-based adsorbents, J. Mol. Liq. 204 (2015) 255-263.

[8] Ihsanullah, F. A. A. Khaldi, B. A. Sharkh, A. M. Abulkibash, M. I. Qureshi, T. Laoui, M. A. Atieh, Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes, Desalin. water treat. (2015). doi: 1 0.1080/19443994.2015.1021847.

[9] C. Chen, J. Hu, D. Shao, J. Li, X. Wang, Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II), J. Hazard. Mater. 164 (2009) 923–928.

[10] Z.C.Di, Y.H. Li, Z.K. Laun, J. Liang, Adsorption of chromium(VI) ions from water by carbon nanotubes, Adsorpt. Sci. Technol. 22 (2004) 467–474.

[11] S.G.Wang, W.X. Gong, X.W. Liu, Y.W. Yao, B.Y. Gao, Q.Y. Yue, Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes, Sep. Purif. Technol. 58 (2007) 17–23.

[12] C. Chen, X. Wang X, Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes, Ind. Eng. Chem. Res. 45 (2006) 9144–9149.

[13] C.L. Chen, X.K. Wang, M. Nagatsu, Europium adsorption on multiwall carbon nanotube/iron oxide magnetic composite in the presence of polyacrylic acid, Environ. Sci. Technol. 43 (2009) 2362–2367.

[14] C.H. Chen, C.C. Huang, Hydrogen adsorption in defective carbon nanotubes, Sep. Purif. Technol. 65 (2009) 305–310.

[15] A. Gaur, M. Shim, Substrate-enhanced O_2 adsorption and complexity in the Raman G-band spectra of individual metallic carbon nanotubes, Phys. Rev. B. 78 (2008) 1254221-1254227.

[16] J. Goering, E. Kadossov, U. Burghaus, Adsorption kinetics of alcohols on single-wall carbon nanotubes: an ultrahigh vacuum surface chemistry study, J. Phys. Chem. C. 112 (2008) 10114–10124.

[17] H. Hyung, J.H. Kim, Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters, Environ. Sci. Technol. 42 (2008) 4416–4421.

[18] Ihsanullah, H.A. Asmaly, T.A. Saleh, T. Laoui, V.K. Gupta, M.A. Atieh, Enhanced adsorption of phenols from liquids by aluminum oxide/carbon nanotubes: Comprehensive study from synthesis to surface properties, J. Mol. Liq. 206 (2015) 176-182.

[19] H. A. Asmaly, B. Abussaud, Ihsanullah, T. A. Saleh, V. K. Gupta, M. A. Atieh, Ferric oxide nanoparticles decorated carbon nanotubes and carbon nanofibers: from synthesis to enhanced removal of Phenol, J. Saudi Chem. Soc. 19 (2015) 511-520.

[20] B.S. Lalia, F. E. Ahmed, T. Shah, N. Hilal, R. Hashaikeh, Electrically conductive membranes based on carbon nanostructures for self-cleaning of biofouling, Desalination 360 (2015) 8–12.

[21] J.K. Holt, A. Noy, T. Huser, D. Eaglesham, O. Bakajin, Fabrication of a carbon Nanotube-embedded silicon nitride membrane for studies of nanometer-scale mass transport, Nano Lett. 4 (2004) 2245-2250.

[22] S.Li, G. Liao, Z. Liu, Y. Pan, Q. Wu, Y. Weng, X. Zhang ,Z. Yang, O.K.C. Tsuid, Enhanced water flux in vertically aligned carbon nanotube arrays and polyethersulfone composite membranes, J. Mater. Chem. A. 2 (2014) 12171-12176.

[23] M. Majumder, N. Chopra, R. Andrews, B.J. Hinds, Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes, Nature 438 (2005) 44-44.

[24] J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes, Science 312 (2006) 1034-1037.

[25] P.S. Goh, A.F. Ismail, B.C. Ng, Carbon nanotubes for desalination: Performance evaluation and current hurdles, Desalination 308 (2013) 2–14.

[26] B.J. Hinds, N. Chopra, R. Andrews, V. Gavalas, L.G. Bachas, Aligned Multiwalled Carbon Nanotube Membranes, Science 303 (2004) 62-65.

[27] S.A. Miller, V.Y. Young, C.R. Martin, Electroosmotic Flow in Template-Prepared Carbon Nanotube Membranes, J. Am. Chem. Soc. 123 (2001) 12335-12342.

[28] W. Chengwei, L. Menke, P. Shanlin, L. Hulin, Well-aligned carbon nanotube array Membrane synthesized in porous alumina template by chemical vapor deposition, Chin. Sci. Bull. 45 (2000) 1373–1376.

[29] A. Srivastava, O.N. Srivastava, S. Talapatra, R. Vajtai, P.M. Ajayan, Carbon nanotube Filters, Nat. Mater. 3 (2004) 610–614.

[30] L.F. Dumee, K. Sears, J. Schütz, N. Finn, C. Huynh, S. Hawkins, M. Duke, S. Gray, Characterization and evaluation of carbon nanotube Bucky-Papermembranes for direct contact membrane distillation, J. Membr. Sci. 351 (2010) 36–43.

[31] R. Andrews, D. Jacques, A.M. Rao, F. Derbyshire, D. Qian, X. Fan, E.C. Dickey, J. Chen, Continuous production of aligned carbon nanotubes: A step closer to commercial realization, Chem. Phys. Lett. 303 (1999) 467–474.

[32] S. Majeed, D. Fierro, K. Buhr, J. Wind, B. Du, A.B.D. Fierro, V. Abetz, Multi-walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes, J. Membr. Sci. 403-404 (2012) 101– 109.

[33] D.L. Arockiasamy, J. Alam, M. Alhoshan, Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications, Appl. Water Sci. 3 (2013) 93–103.

[34] H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite, J. Membr. Sci. 362 (2010) 374–383.

[35] P. Shah, C.N. Murthy, Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal, J. Membr. Sci. 437 (2013) 90–98.

[36] Ihsanullah, T. Laoui, A.M. Al-.Amer, A. B. Khalil, A. Abbas, M. Khraisheh, M. A. Atieh, Novel anti-microbial membrane for desalination pretreatment: A silver nanoparticle-doped carbon nanotube membrane, Desalination 376 (2015) 82-93.

[37] G.T. Pham, Y.B. Park, S. Wang, Z. Liang, B. Wang, C. Zhang, P. Funchess. L. Kramer, Mechanical and electrical properties of polycarbonate nanotube buckypaper composite Sheets, Nanotechnology 19 (2008) 325705.

[38] G.T. Pham, Y.B. Park, S. Wang, Z. Liang, B. Wang, C. Zhang, P. Funchess, L. Kramer, Mechanical and electrical properties of polycarbonate nanotube buckypaper composite Sheets, Nanotechnology 19 (2008) 325705.

[39] Y. Ma, F. Shi, Z. Wang, M. Wu, J. Ma, C. Gao, Preparation and characterization of PSf/clay nanocomposite membranes with PEG 400 as a pore forming additive, Desalination 286 (2012) 131–137.

[40] K. Ebert, D. Fritsch, J. Koll, C. Tjahjawiguna, Influence of inorganic fillers on the compaction behaviour of porous polymer based membranes, J Membr Sci. 233 (2004) 71–78.

[41] S. Majeed, D. Fierro, K. Buhr, J. Wind, B. Du, A.B.D. Fierro, V. Abetz, Multi-walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes, J Membr Sci. 403-404 (2012) 101– 109.

[42] D.L. Arockiasamy, J. Alam, M. Alhoshan, Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications, Appl Water Sci. 3 (2013) 93–103.

[43] H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite, J Membr Sci. 362 (2010) 374–383.

[44] P. Shah, C.N. Murthy, Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal, J Membr Sci. 437 (2013) 90–98.

[45] S.J. Oh, N. Kim, Y.T. Lee, Preparation and characterization of PVDF/TiO_2 organic– inorganic composite membranes for fouling resistance improvement, J. Membr. Sci. 345 (2009) 13–20.

[46] R.A. Damodar, S.J. You, H.H. Chou, Study the self cleaning, antibacterial and photo catalytic properties of TiO_2 entrapped PVDF membranes, J. Hazard. Mater. 72 (2009) 1321–1328.

[47] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized Al_2O_3-particle addition on PVDF ultrafiltration membrane performance, J. Membr. Sci. 276 (2006) 162–167.

[48] F. Liu, M.R.M. Abed, K. Li, Preparation and characterization of poly(vinylidene fluoride)(PVDF) based ultrafiltration membranes using nano γ-Al_2O_3, J. Membr. Sci. 366 (2011) 97–103.

[49] A. Bottino, G. Capannelli, A. Comite, Preparation and characterization of novel porous PVDF-ZrO_2 composite membranes, Desalination 146 (2002) 35–40.

[50] S.P. Nunes, K.V. Peinemann, K. Ohlrogge, A. Alpers, M. Keller, A.T.N Pires, Membranes of poly(ether imide) and nano dispersed silica, J. Membr. Sci. 157 (1999) 219–226.

[51] L. Liu, D. Y. W. Di, H. Park, M. Son, H. G. Hurand H.Choi, Improved antifouling performance of polyethersulfone (PES) membrane via surface modification by CNTs bound polyelectrolyte multilayers, RSC Adv. 5 (2015) 7340-7348.

CHAPTER 2

HEAVY METAL REMOVAL FROM AQUEOUS SOLUTION BY ADVANCED CARBON NANO TUBES: CRITICAL REVIEW OF ADSORPTION APPLICATIONS

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Abstract

The scarcity of water, especially in arid and semi-arid regions of the world is exerting great pressure on resources and establishing more need to provide good quality water for human and other consumptions. Water recovery/recycle/reuse has proven to be effective and successful in creating a new and reliable water supply. Accordingly, attention is being paid to the effective treatment of alternative sources of water (apart from fresh water) such as seawater, storm water, wastewater (e.g. treated sewage water), and industrial wastewater. In this review, the use of carbon nanotubes (CNTs), member of the fullerene structural family, is considered with special focus on the removal of heavy metals from water (lead, chromium, cadmium, arsenic, copper, zinc and nickel). A critical review into the adsorption behavior and use of the CNTs is given with attention being paid to the effects of surface modifications on the adsorption behavior and subsequent heavy metal removal. A review of the effect of a number of key variables including pH, CNTs dosage, time, ionic strength, temperature and surface charge are given. It will be demonstrated that, surface modification enhances positively the adsorption capacity of CNTs towards cadmium, chromium, lead, mercury, copper, zinc, cobalt and nickel as did the solution pH. CNTs have been proven to an excellent adsorbent for the removal of different heavy metals from water. However, most of the applications of CNTs are on lab scale in batch experiments. In spite of high costs, CNTs are expected to be a promising adsorbent in the future due to its high adsorption capacity compared to many traditional adsorbents. Researchers are also in quest of novel environment friendly techniques for the surface modification of CNTs to further improve their properties. Still, the feasibility of CNTs application in large scale treatment needs to

be further studied. Effective techniques for regeneration/reuse of CNTs also need to be explored yet. One of the main hurdles that limit the applications of CNTs in large scale operation is the cost of CNTs. Future research works on developing a cost-effective way of CNT production and testing the toxicity of CNTs and CNT-related materials are recommended.

Keywords: *Carbon nanotubes, heavy metals, adsorption, water treatment*

2.1 Introduction

Heavy metals in general have a density greater than 5 g per cubic centimeter and atomic weights between 63.5 and 200.6 [1-3]. The pollution of water due to release of heavy metals into ecosystem metals has been causing worldwide concern. The main sources of heavy metals are the wastewaters from modern chemical industries such as metal plating facilities, battery manufacturing, fertilizer, mining, paper and pesticides, metallurgical, mining, fossil fuel, tannery and production of different plastics such as polyvinyl chloride. The rapid industrialization during recent years has greatly contributed to heavy metals release in to environment [4]. Heavy metals tend to accumulate in living organisms as they are not biodegradable, unlike organic contaminants. Toxic heavy metals of particular concern, in treatment of industrial wastewaters include lead, chromium, cadmium, mercury, arsenic, nickel, copper and zinc.

The toxic effects of heavy metals such as arsenic, cadmium, chromium, mercury, zinc and lead on human health have been investigated extensively. The possible symptoms of the toxic metals includes high blood pressure, speech disorders, fatigue, sleep disabilities, aggressive behavior, poor concentration, irritability, mood swings, depression, increased allergic reactions, autoimmune diseases, vascular occlusion, and memory loss [5]. Heavy metals can also disrupt the human cellular enzymes, which run on nutritional minerals such as magnesium, zinc, and selenium. Some of the toxic heavy metals that can be harmful to human body include cadmium, lead, arsenic and mercury. Though, our body needs some heavy metals such as manganese, iron, chromium, copper and zinc but still presence in large quantities of these metals may be extremely dangerous [5-7]. This paper

reviews the removal of selected metal ions (Lead, chromium, cadmium, arsenic, copper, zinc and nickel) from water using carbon nanotubes.

Table 2-1 summarizes the allowable concentrations limits for the selected heavy metals, as reported by U.S. Environmental Agency (U.S. EPA) and World Health Organization (WHO) [8-9].

Table 2-1: WHO and US EPA limitations of selected heavy metal in drinking water [6-7]

Contaminant	**EPA limitations**		**WHO provisional guideline value (mg/L)**
	Maximum contamination level (MCL) (mg/L)	**Maximum contamination limit goal (MCLG) (mg/L)**	
Lead	0.015	0	0.01
Chromium	0.1	0.1	0.05
Cadmium	0.005	0.005	0.003
Arsenic	0.010	0	0.01
Mercury	0.002	0.002	0.006
Copper	1.3	1.3	2
Zinc	5	-	3
Nickel	-	-	0.07

2.2 Heavy Metals in Water: Sources of Contaminations and their Toxic Effects

2.2.1 Lead

Lead is a non-biodegradable hazardous heavy metal that easily accumulates in human body. The major source of lead in human body is the drinking water, containing substantial amount of lead. Initially it can enter the body through the digestive tract and lungs and carried spread by blood throughout the body. Presence of large quantity of lead in drinking water will cause anaemia, cancer, renal kidney disease, nervous system damage and mental retardation [1-5].

2.2.2 Chromium

Chromium is a metal found in natural deposits as ores containing other elements such as ferric chromite ($FeCr_2O_4$), crocoite ($PbCrO_4$), and chrome ochre (Cr_2O_3). Chromium is considered one of the earth crust's most abundant elements and it is estimated to be the sixth most abundant transition metal [10]. It is a well-known highly toxic metal in drinking water. Chromium naturally found in different oxidation states ranging from 2+, 3+ and 6+, with the trivalent Cr(III) and hexavalent Cr(VI) are the most stable forms in nature. Cr(III) is much less toxic than Cr(VI) and it is an essential element in human bodies [11]. In contrast, Cr(VI) is extremely toxic and found in various industrial waters and can cause severe diarrhea, vomiting, pulmonary congestions liver and kidney damage [12-14]. Chromium metal is used in textile industries, electroplating, leather tanning, metal finishing, and chromate preparation [15]. Therefore, the potential source of

chromium to drinking water contamination is industrial wastewater discharge to environment. The industrial sources include cooling tower blowdown, electroplating, metal plating and coating operations, etc. Cr(VI) is present mainly in the form of dichromate ($Cr_2O_7^{2-}$) and chromate (CrO_4^{2-}) ions. Depending on solution pH, Cr(VI) can exists in water as dichromate ($Cr_2O_7^{2-}$) ions, chromate ion (CrO_4^{2-}), hydrogen chromate ion ($HCrO_4^-$) and chromic acid (H_2CrO_4) [16].

2.2.3 Cadmium

Cadmium is a heavy metal found in natural deposits containing other elements. This element is highly toxic and considered as one of the major priority pollutant in drinking water. Cadmium was found to accumulate primarily in the kidneys and has a relatively long biological half-life in human bodies of 10 to 35 years [17-18]. As a drinking water pollutant, kidney is the main target organ for cadmium toxicity.

Cadmium metal is mainly used in steel and plastics industries. Therefore, the potential sources of cadmium contamination in drinking water contamination are the industrial wastewater discharge to environment. Other industrial sources of cadmium contamination include cooling tower blow down, electroplating, metal plating and coating operations, etc. Cadmium is also used in nickel-cadmium batteries, in Cd-Te thin film solar cells and in pigments. One major source for non-industrial sourced cadmium contamination in drinking-water is impurities in the zinc of galvanized pipes and some metal fittings [19].

2.2.4 Arsenic

Arsenic present in the water originates from natural resources and human activity. They are released into the surface ground water by means of geological formation that happens in sedimentary rocks, geothermal water and from weathered volcanic rocks. Human

activities like mining, manufacturing, metallurgy, wood preservation and as pesticides also introduce arsenic into the water bodies [20].

The National Arsenic Occurrence Survey investigated that more than 5 µg/L arsenic are present in 21 percent of the ground water and 10 percent of the surface water [21-22]. The reason that put concerns with arsenic in drinking water was that the majority of the population who has been exposed to arsenic in drinking water reported cases of cancer-based health concerns. High levels of arsenic contaminant have been found in Taiwan, India and West Bengal where they have been exposed to much higher levels than the maximum possible concentration of 10 µ/L [23]. Skin cancers; lung bladder and kidney cancers and other internal tumors; vascular diseases and diabetes are the diseases that are reported by population drinking arsenic contaminated water. There has been also reported case of infant mortality and weight loss of new born babies [24-26]. These cases are only a correlation in the study as the main mechanism of the toxicology levels of arsenic have not been studied thoroughly but for sure both the individual and the population has been susceptible to the poisonous effects of arsenic contaminant water [27-31].

2.2.5 Mercury

Mercury bioavailability and toxicity is dictated by its species which in turn influenced by the natural chemical and biological processes. Mercury may change between different states and species in its cycle, but its simplest form is elemental mercury which itself is harmful to humans and the environment. After liberation of mercury from mineral deposits, fossil fuel or ores, the possible sites of its accumulation are bottom sediments, water bodies and earth's surface soils [32]. Being an element, mercury cannot be broken down or degraded into harmless substances. Once mercury has been liberated from either

ores or and hidden in the earth's crust and released into the biosphere, it can be highly mobile, cycling between the earth's surface and atmosphere. Although most mercury occurs in the inorganic form, methyl-mercury is the most toxic and readily bio-accumulated form of mercury. The major targets are the nervous system upon short-term exposure; while kidneys upon long-term exposure. The potential toxic effects of mercury include damage to kidneys, reproductive systems, immune, hematologic, cardiovascular, respiratory system and brain [32]. Consequently more stringent regulatory controls have been imposed for mercury in many countries. The average mercury levels in urine and blood of human population are approximately 4 μg/L and 8 μg/L, respectively. However, this level may be high up to 200 μg/L in individuals whose diet consists of substantial amounts of fish [33].

2.2.6 Copper

Copper has a number of applications in industrial and agricultural processes. Copper can be released into the environment from many sources. Drinking water can be a potential source for an intense copper exposition. Copper is highly toxic for drinking water, and mercury is the only metal more toxic than copper [34-37]. Although copper is important for animal metabolism. However, the excessive ingestion of copper brings about serious treats, such as increased blood pressure and respiratory rates damaged in kidney and liver, convulsions, cramps, vomiting, or even death [3, 38-39].

2.2.7 Zinc

Zinc plays a vital role in regulating many biochemical processes and physiological functions of living tissue. However, the presence of zinc in excess causes eminent health problems, such as stomach nausea, skin irritations, cramps, vomiting, and anemia [3].

The industrial sources of zinc include brass platting, wood pulp production, ground and newsprint paper production, steel works with galvanizing lines, zinc and brass metal works. Waste concentrations of zinc range from less than 1 to more than 48,000 mg. L^{-1} in various waste streams described in the literature. Zinc is released into environment from sediment remobilization or entrainment, agricultural activities, groundwater intrusion or from a combination of these sources [40].

2.2.8 Nickel

Nickel is a non-biodegradable toxic heavy metal ion present in wastewater. The main source of nickel pollution in the water derives from a number of industrial production processes such as battery manufacturing, production of some alloys, zinc base casting, printing, electroplating and silver refineries [41-42]. The toxic effects of nickel include dry cough, bone nose, and lung cancer, cyanosis, rapid respiration, shortness of breath, tightness of the chest, chest pain, and nausea [41-42]. Table 2-2 provides summary of the possible sources, toxic effects and available treatment techniques for these metals.

Table 2-2: Sources of contaminations and potential toxic effects of some heavy metals

Heavy metal	Sources of contaminations	Potential toxic effects	Available treatment techniques	References
Lead	i. Paint ii. Pesticides iii. Smoking iv. Automobile emissions v. Burning of coal vi. Mining	i. Anaemia ii. Cancer iii. Renal kidney disease iv. Nervous system damage v. Mental retardation vi. Impaired intellectual ability and behavioral problems in children	i. Reverse osmosis ii. Ion exchange iii. Membrane separation iv. Filtration v. Adsorption vi. Cementation vii. Chemical precipitation	[1-5, 43-55]
Chromium	i. Industrial wastewater discharge to environment. ii. Cooling tower blowdown iii. Electroplating iv. Metal plating and coating operation	i. Severe diarrhea ii. Vomiting iii. Pulmonary congestions liver and kidney damage	i. Membrane technologies ii. Ion exchange iii. Coagulation iv. Floatation v. Solvent extraction vi. Cyanide treatment vii. Adsorption	[10-16, 56]
Cadmium	i. Steel and plastics industries. ii. Cooling tower blow down iii. Electroplating, metal plating and coating operations, etc. iv. Nickel-cadmium batteries v. Cd-Te thin film solar cells and	i. Damage to kidney ii. Cancers iii. Bronchiolitis, COPD, emphysema, fibrosis iv. Skeletal damage	i. Coagulation ii. Ion-exchange iii. Precipitation iv. Softening, v. Membrane separation	[17-19, 57-58]

	pigments. vi. Zinc of galvanized pipes vii. Welding viii. Fertilizers ix. Nuclear emission plants			
Arsenic	i. Pesticides ii. Fungicides iii. Sedimentary rocks, geothermal water and from weathered volcanic rocks iv. Human activities like mining, manufacturing, metallurgy and wood preservation	i. Skin cancers ii. Lungs, bladder and kidney, cancer and other internal tumors iii. Vascular diseases and diabetes. iv. Infant mortality and weight loss of new born babies v. Hearing loss vi. Reproductive toxicity vii. Hematologic disorders viii. Neurological diseases ix. Developmental abnormalities and neurobehavioral disorders	i. Coagulation ii. Lime softening iii. Iron-manganese removal iv. Ion exchange v. Activated alumina vi. Reverse osmosis vii. Micro or ultrafiltration	[20-31, 59-63]
Mercury	i. Mineral deposits ii. Fossil fuel or ores iii. Pesticides iv. Batteries v. Paper industry	i. Damage to kidneys ii. Reproductive systems iii. Immune, hematologic, cardiovascular, respiratory system and brain	i. Precipitation/Co-precipitation ii. Bioremediation iii. Adsorption iv. Ion exchange v. Membrane filtration	[32-33, 64-66]
Copper	i. Pesticides industry	i. Increased ii. blood pressure and	i. Ion exchange ii. Reverse osmosis	[3, 34-39,

	ii. Mining iii. Metal piping iv. Chemical industry	respiratory rates iii. Damaged in kidney and liver iv. Convulsions, cramps, vomiting, or even death	iii. Membrane technologies iv. Chemical precipitation v. Electrochemical treatment	67-72]
Zinc	i. Brass platting ii. Wood pulp production iii. Ground and newsprint paper production iv. Steel works with galvanizing lines v. Zinc and brass metal works. vi. Refineries vii. Plumbing	i. Stomach nausea ii. Skin irritations iii. Cramps iv. Vomiting and anemia	i. Precipitation ii. Membrane processes iii. Ion exchange resins iv. Adsorption	[3, 40]
Nickel	i. Battery manufacturing ii. Production of some alloys iii. Zinc base casting iv. Printing v. Electroplating vi. Silver refineries	i. Dry cough ii. Bone nose, and lung cancer iii. Cyanosis, rapid respiration iv. Shortness of breath v. Tightness of the chest, chest pain vi. Nausea and vomiting vii. Dizziness	i. Reduction and precipitation ii. Coagulation and flotation iii. Adsorption iv. Ion exchange v. Membrane technology vi. Electrolysis	[41-42, 73-81]

2.3 Available Techniques for the Removal of Heavy Metals from Water

A number of methods have been employed for the removal of heavy metals from water. The selection of a particular treatment method is mainly based on the economics and level of initial concentrations of the heavy metals. In water treatment processes, the heavy metals are usually removed during the chemical and physical treatment processes. This raw water could be seawater, brackish ground water, or surface water.

The conventional methods that have been used to remove the metal ions include oxidation, reduction, bioremediation, reverse osmosis, electrochemical treatment, coagulation, lime softening, precipitation, membrane filtration, ion exchange and adsorption [3, 34-37, 67-72]. Table 2-3 summarizes the advantages and disadvantages of different techniques for heavy metals removal. All these methods have their own capabilities and limitations. For example, precipitation/co-precipitation has the disadvantage of hazardous waste production that needs to be treated. Membrane filtration is another treatment method but its cost and generation of larger volume of rejected residuals limits its applications. Ion exchange has high removal efficiency but regeneration of the resins cause serious secondary pollution. Electrodialysis has high separation selectivity but high operational cost due to energy consumption. Photocatalysis has the disadvantage of long duration. Coagulation and flocculation are undesirable because of increased sludge volume generation and flotation has the disadvantage of high initial, operation and maintenance cost.

Adsorption is proven to be economical and effective method for the removal of a number of contaminates from water [36-37,40-42]. Furthermore, the employed adsorbent can be regenerated by suitable desorption process [48, 82].

Several adsorbents have been employed for the adsorption of metal ions such as activated carbon [7,15,17, 64-66, 73, 83], crab shell [84], fly ash [85-86], granular biomass [74], peat [87], modified chitosan [75], sewage sludge ash [88], peanut hulls [76], activated carbon cloths [77], zeolite [89], sugar beet pulp [78], biomaterials [19,90], kaolinite [79], olive stone waste [80] recycled alum sludge [91], manganese oxides [92], bagasse [81], and resins [93]. However, these adsorbents suffer from low adsorption capacities or removal efficiencies of metal ions. Therefore, researchers are in quest of exploring the new promising adsorbents.

In recent years, CNTs have been employed extensively as a new adsorbent for the removal of a number of heavy metals from water. CNTs have been used to remove cadmium [17, 57-58], chromium [14-15, 101-102], lead [103-105], nickel [106-108], copper [109-111], mercury [112-113], arsenic [114-115], zinc [116-117] and cobalt [118-120]. The results of these studies confirmed that CNTs are an excellent adsorbent for the removal of heavy metal from aqueous solutions.

Table 2-3: Advantages and disadvantages of the current techniques for heavy metals removal

Method	Advantages	Disadvantages	References
Ion exchange	i. High treatment capacity ii. High removal efficiency iii. Fast kinetics	i. High cost due to synthetic resins ii. Regeneration of the resins cause serious secondary pollution	[3, 94]
Adsorption	i. Easy operating conditions ii. High metal binding capacities iii. Having wide pH range iv. Low-cost	i. Production of waste products ii. Low selectivity	[2-3, 68, 95]
Chemical precipitation	i. Simple operation ii. Low capital cost	i. Sludge generation ii. Extra operational iii. Cost for sludge disposal iv. Ineffective for treatment of water with low concentration of heavy metals	[67, 96]
Membrane filtration	i. High separation selectivity ii. Small space requirement iii. Low pressure requirement	i. High operational cost due to membrane fouling ii. Process complexity iii. Low permeate flux	[35, 72, 96]
Electrodialysis	i. High separation selectivity	i. High operational cost due to energy ii. Consumption and membrane fouling	[2, 97]
Photocatalysis	i. Removal of metals and organic pollutant simultaneously ii. Less harmful by-products	i. Limited applications ii. Long duration time	[2, 98]

Coagulation and flocculation	i. Remove the turbidly in addition to heavy metal removal ii. Produced sludge with good sludge settling and dewatering characteristics	i. Increased sludge volume generation ii. Coagulation flocculation can't treat the heavy metal wastewater and must be followed by other treatment techniques	[3, 96, 99]
Flotation	i. High metal selectivity ii. High removal efficiency iii. High overflow rates iv. Low detention periods v. Low operating cost vi. Production of more concentrated sludge	i. High initial capital cost ii. High maintenance and operation costs	[3,96, 100]

2.4 Carbon Nanotubes

Carbon has the property to exist in many molecular forms, known as allotropes of carbon. These allotropes can be considered as different structural modifications of carbon element. Carbon nanotubes (CNTs) are composed of cylindrical graphite sheets (allotropic form of carbon) rolled up in a tube like structure [121]. Single-walled carbon nanotubes (SWCNTs) have cylindrical shape consisting of a single shell of graphene. On the other hand, multi-walled carbon nanotubes (MWCNTs) are composed of multiple layers of graphene sheets. Fig. 2-1 shows structure of (a) Multiwall carbon nanotubes (MWCNTs) and (b) Single walled carbon nanotubes (SWCNTs) [122], while Fig. 2-2 represents different structure of SWCNTs based on rolling of graphene sheets. The structure of the nanotubes is based on the orientation of tube axis with respect to hexagonal lattice and can be specified through its chiral vector, represented by chiral

indices (n, m). The origin of armchair (n=m) and zigzag (n=0) nanotubes structure is from the geometric arrangements of carbon atoms at the seam of the cylinders. While nanotubes structure with two enantiomers with right and hand side halcity (n≠m) are chiral [123]. CNTs were discovered in 1991 by Sumio Iijima of NEC Laboratory in Tsukuba, Japan, using arc-discharge method and they were characterized by High-Resolution Transmission Electron Microscope (HRTEM) [124]. Chemical bonding in nanotubes is composed entirely of sp^2 bonds, which are stronger than the sp^3 bonds found in alkanes and provide nanotubes a unique strength [125].

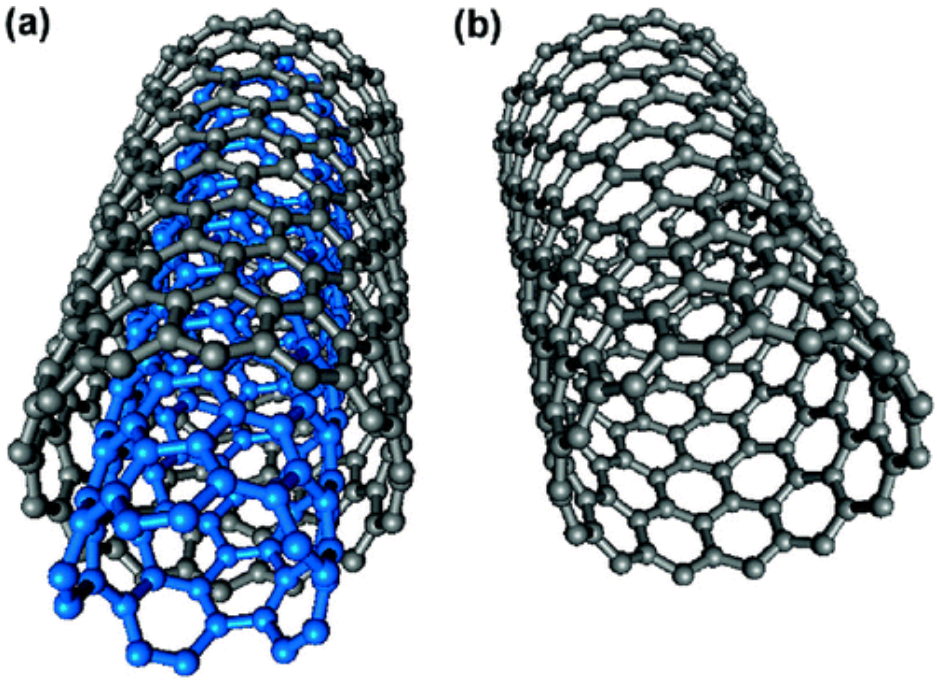


Figure 2-1: Structure representations of (a) MWCNTs (b) SWCNTs [117] (Reprint permission from American Chemical Society)

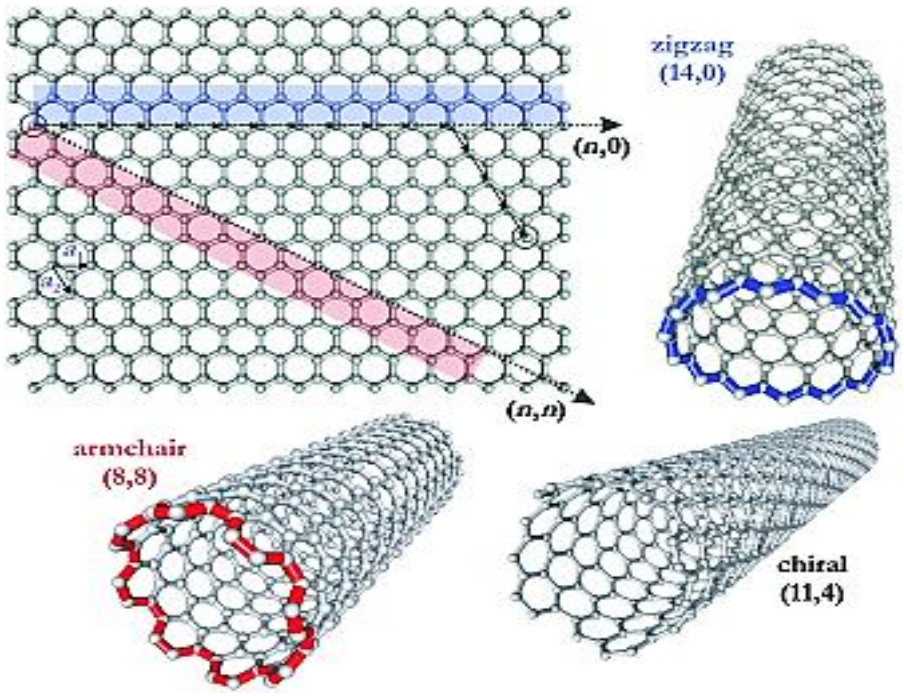


Figure 2-2: Roll-up of a graphene sheet leading to the three different types of CNTs [118] (Reprint permission from John Wiley and Sons)

2.4.1 Carbon Nanotubes in Water Treatment

CNTs have been widely employed for the removal of various contaminants from aqueous solutions due to their large surface area, light mass density, high porous and hallow structure, and strong interaction between the pollutant molecules and CNTs [101-106,126-130].

Various experimental studies have reported the adsorption of heavy metal ions [57-58, 101-120], small molecules [131-134], organic chemicals [135-139] and radionuclides [140-143] on different CNTs. Adsorption properties of CNTs depend on their purity, porosity, surface functional groups, surface area, site density and type of CNTs (open ended or closed ended). Possible sites for the adsorption of different contaminants (see Fig. 2-3) in CNT bundles [131,140-144] are (1) internal sites – the hollow interior of individual nanotubes. However, these sites can be accessed only by removing the caps

and unblocking the open ends; (2) interstitial channels (ICs) – the pathways between individual nanotubes in the bundles; (3) grooves – it includes the surface of the outermost nanotubes and grooves present on the periphery of a nanotube bundle and (4) outside surface – the curved surface of individual nanotube on the outside of the nanotube bundles. Numerous studies have been conducted to observe the adsorption process of adsorbate molecules on different sites [145-149]. Results of these studies confirmed that most of the adsorption takes place on the interstitial channels (ICs), outer surface sites and on the grooves [150-155].

In general, both ends of produced CNTs are closed initially. Therefore, the possible sites for initial adsorption are interstitial channels and grooves between adjacent tubes bundles, as observed for CH_4 and Kr adsorption [146]. However, only the grooves are able to accommodate bigger molecules such as Xe, CF_4 and SF_6 [147]. In second stage, the adsorption proceeds on external walls followed by the accumulation of molecules on axial sites inside the nanotubes [156]. However, it has been observed that the time required for adsorption to reach equilibrium value is much smaller for external sites (outer surfaces and grooves) than the internal sites (inside the tube and interstitial channels) under the same conditions. This behavior is expected due to easy accessible and exposed external sites to the adsorbing material; and by considering the resistance to diffusion of adsorbents to the interior sites [157-158]. Adsorption process also depends on the number of open and unblocked nanotubes. It has been investigated that opening the ends of CNTs increases the number of adsorption sites, thus enhances the saturation capacity and kinetic rate [159-160].

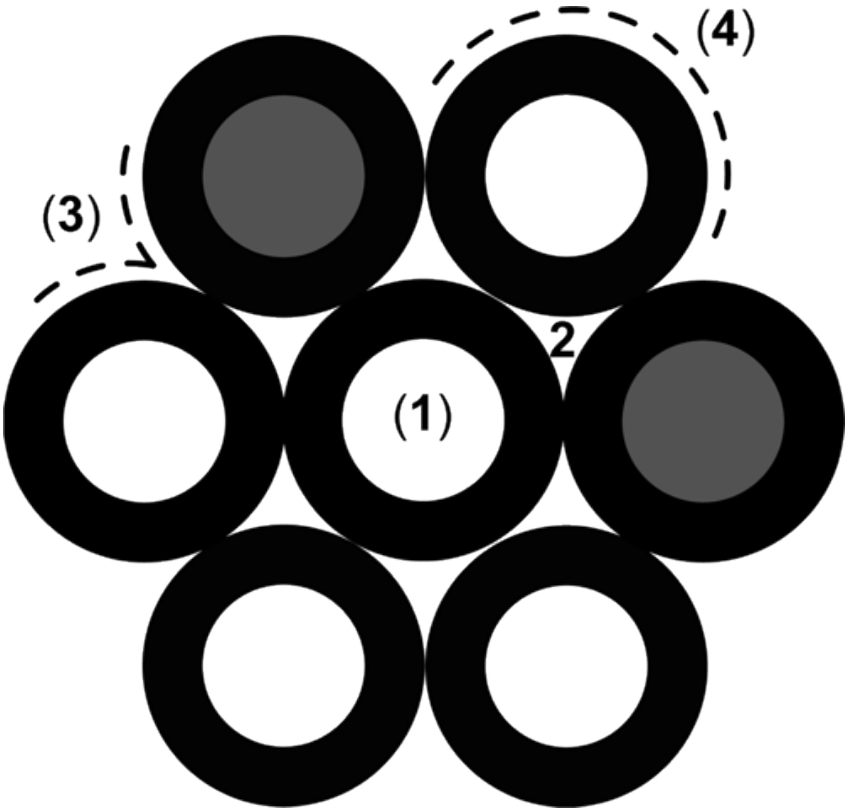


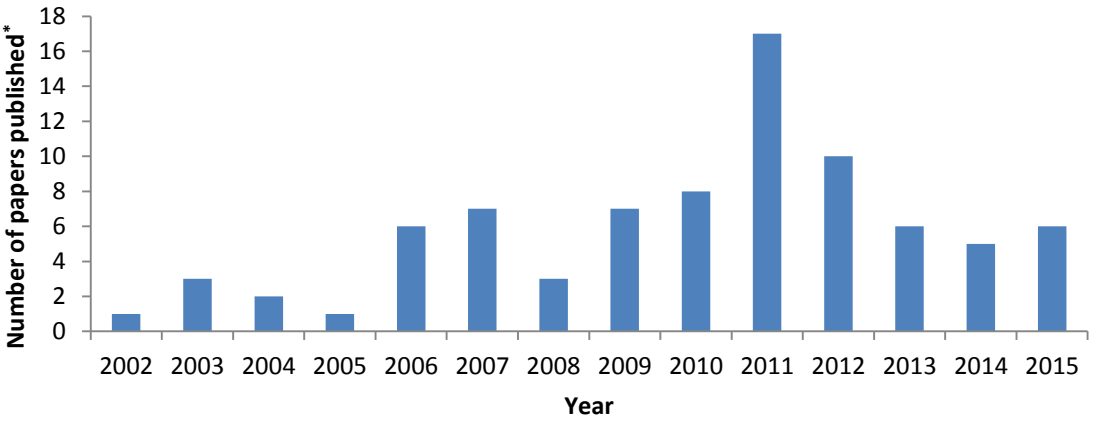
Figure 2-3: Different adsorption sites on SWCNTs: (1) Internal, (2) Interstitial channel (ICs), (3) External groove site, and (4) External surface [149] (Reprint permission from American Chemical Society)

2.4.2 Carbon Nanotubes Adsorbents

In recent years, CNTs have been employed extensively as a new adsorbent for the removal of a number of heavy metals from water [161-184]. Table 2-4 shows the summary of various studies for the adsorption of different heavy metals using different types of carbon nanotubes. It can be observed that in most of the studies, the maximum adsorption capacity is determined using Langmuir isotherm model. Furthermore, the adoption capacity of the acid modified CNTs is higher, almost in all studies, as compared to the raw CNTs. This might be due to electrostatic interaction between the negative charge on the CNTs surface after acid treatment and the divalent heavy metal ions. CNTs are also employed in combination with other nanoparticles with the aim to improve the

removal efficiency. Modified CNTs has shown excellent removal efficiency for the heavy metal ions. Table 2-4 also summarizes the interaction mechanisms between the heavy metals and CNTs for the individual processes.

Fig. 2-4 represents summary of the research articles published in recent years that reported CNTs as an adsorbent for the removal of heavy metals from water. It can be observed that the research propagates gradually from 2002-2011. This might be due to considerable attention of researchers towards CNTs as a new adsorbent. The recent four years from 2012-2015 show a slight decline in number of papers. This may be attributed to exploration of the other potential applications of CNTs beside heavy metal adsorption.



*These numbers are based on the publications cited in this review.

Figure 2-4: The progress of CNTs applications for heavy metals removal from 2002-2015

Table 2-4: The adsorption capacities of CNTs for some heavy metal ions adsorption

Adsorbates	Adsorbents	Adsorption capacity, Q (mg/g)		Conditions	Interaction mechanism	Model used	References
		Calculated from model	***Experimental***				
Pb(II)	Acidified MWCNTs	17.44	11.2	pH 5, Initial concentration = 10 mg/L, adsorbent dosage=0.05 g	Ion exchange	Langmuir	[47]
	Acidified MWCNTs	N/A	30.32	pH 5, Initial concentration= 30 mg/L, T= 298 K	N/A	Freundlich	[48]
	Oxidized CNTs	N/A	82.6	pH 5, Concentration =10 mg/L	N/A	Experimental	[49]
	HNO_3-modified CNTs	97.08	82	pH 5, Initial concentration =10 mg/L, Room Temperature	Ion exchange	Langmuir	[52]
	CNTs	102.04	37.594	pH 5, CNTs dosage =10 mg, contact time= 80 min	Chemi-sorption	Langmuir	[103]
	Acidified MWCNTs	N/A	91	Initial concentration =50 mg/L, *T*= 298 K	Chemical adsorption	Experimental	[104]
	Nitrogen-doped magnetic CNTs	N/A	6.74 mmol/g	pH 8	Chemical adsorption	Experimental	[116]
	Acidified MWCNTs	49.71	85	pH 5, Initial concentration= 50 mg/ L,T= 298 K	Physical adsorption	Langmuir	[161]
	Magnetic-function-alized MWCNTs	N/A	N/A	pH 6, Initial concentration =100 mg/ L	N/A	Experimental	[162]
	MnO_2/CNTs	78.74	N/A	pH 5, Concentration	Electrostatic interaction,	Langmuir	[163]

				=30 mg/L, T= 298 K	surface complex-ation		
	3-mercaptopropyltriethoxysilane (MPTS) grafted MWCNTs/ Fe_3O_4	65.40	42.12	pH 6.5, Initial concentration = 50 mg/L, T= 25 ± 0.2 ^oC	Lewis acid–base interactions	Langmuir	[164]
	Oxidized-MWCNTs	N/A	17	pH 7	N/A	Experimental	[165]
	Oxidized MWCNTs	0.0211 mmol/g	N/A	pH 4.1 ± 0.1, Initial surfactant concentration = 0.83 mmol/L, Adsorbent dosage = 0.75 g/L	Electrostatic, hydrophobic, chemical , π-π interaction	Langmuir	[166]
	TiO_2/ MWCNT composites	137.0	4.63	pH 6, Concentration= 10 mg/L	N/A	Langmuir	[167]
	MWCNTs	33	4.86	pH 6, Concentration=10 mg/L	N/A	Langmuir	[167]
	MWCNTs grafted with 2-vinylpyridine (VP)	37	N/A	pH 6	Ion exchange, electrostatic	Langmuir	[168]
	MWCNTs	15.9	N/A	pH 6	Ion exchange, electrostatic	Langmuir	[168]
	MWCNTs/ Fe_3O_4	22.04	13.04	pH 5.3, Initial concentration = 30 mg/L	Electrostatic, hydrophobic, π-π interaction	Langmuir	[169]
	MWCNTs/ Fe_3O_4 modified with 3-aminopropylt	75.02	37.64	pH 5.3, Initial concentration = 30 mg/L	Electrostatic, hydrophobic, π-π interaction	Langmuir	[169]

	riethoxy-silane (APTS) (MWCNTs/ Fe_3O_4-NH_2)						
	Oxidized CNTs	117.65	101.05	pH 7, Initial concentration = 1200 mg/L, T = 298 K	Chemical interactions	Langmuir	[170]
	SWCNTs	33.55	N/A	pH 5, Initial concentration = 20 mg/L; contact time, 120 min, adsorbent dosage, 50 mg/L, T = 298 ± 1 K	Physisorption	Langmuir	[171]
	SWCNTs-COOH	96.02	N/A	pH 5, Initial concentration = 20 mg/L; contact time, 120 min, adsorbent dosage, 50 mg/L, T = 298 ± 1 K	Chemi-sorption	Langmuir	[171]
	Oxidized MWCNTs	N/A	2.96	pH 9, Initial concentration = 1-20 mg/L, adsorbent dosage = 50 mg	Electrostatic interactions	Freundlich	[172]
Cr(VI)	Oxidized MWCNTs	4.2615 ± 0. 0607	1.0064 ± 0.0065	pH 2.05, Initial concentration= 3 mg/L, T = 20 ± 2 °C	Surface complexation	Langmuir	[14]
	Raw MWCNTs	3.115	1.021	pH 3, Initial concentration=1 mg/L, adsorbent dosage = 75 mg	Electrostatic interactions	Langmuir	[15]
	Acid modified MWCNTs	1.314	0.964	pH 3, Initial concentration=1 mg/L, adsorbent dosage = 75 mg	Electrostatic interactions	Langmuir	[15]
	Raw CNTs	26.88	20.56	pH 7.5, Initial concentration	Ion exchange	Langmuir	[101]

				=33.28 mg/L			
	CNT-AC	N/A	9	pH 2, Initial concentration =0.5 mg/L	N/A	Langmuir	[173]
	Ceria nanoparticles supported on aligned carbon nanotubes (CeO_2/ ACNTs)	31.55	30.2	pH 7, Initial concentration =35.3 mg/L	Ion exchange	Langmuir	[174]
	Acid treated CNTs	249 μmol/g	N/A	pH 7.8	Ion exchange	Langmuir	[175]
	Pristine CNTs	16 μmol/g	N/A	pH 7.8	Ion exchange	Langmuir	[175]
	MWCNTs	13.2	N/A	pH 2.5–4.0, Initial concentration= 20 mg/ L	Electrostatic, cation- π interaction, anion- π interaction	Langmuir	[176]
	Ionic Liquid-function-alized oxi-MWCNTs	85.83	2.57	N/A	Electrostatic, cation- π interaction, anion- π interaction	Langmuir	[176]
Cr(III)	Raw MWCNTs	0.3853	0.3718	pH 7, Initial concentration = 1 mg/L	Electrostatic interactions	Pseudo second order	[11]
	Acid modified MWCNTs	N/A	0.5	pH 7, Initial concentration = 1 mg/L	Electrostatic interactions	Pseudo second order	[11]
	Nitrogen-doped magnetic CNTs	83.752 mmol/g	12.28 mmol/g	pH 8	Chemical adsorption	Langmuir	[116]
Cd (II)	Acid modified	4.35	2.02	pH 7, adsorbent dosage =50 mg	Electrostatic interactions	Langmuir	[17]

	CNTs						
	HNO_3-modified CNTs	10.86	9.2	pH 5, Initial concentration =10 mg/L, Room Temperature	Ion exchange	Langmuir	[52]
	As-grown CNTs	N/A	1.1	pH 5.5, Initial concentration= 4 mg/L	N/A	Experimental	[57]
	H_2O_2 oxidized CNTs	N/A	2.6	pH 5.5, Initial concentration= 4 mg/L	N/A	Experimental	[57]
	HNO_3 oxidized CNTs	N/A	5.1	pH 5.5, Initial concentration= 4 mg/L	N/A	Experimental	[57]
	$KMnO_4$ oxidized CNTs	N/A	11	pH 5.5, Initial concentration= 4 mg/L	N/A	Experimental	[57]
	Ethylenediamine-functionalized MWCNTs	25.70	21.23	Initial concentration= 5 mg/L, T=45^oC	Physi-sorption, Chemi-sorption	Langmuir	[58]
	Oxidized CNTs	24.15	22.32	Initial concentration= 5 mg/L, T=45^oC	Chemi-sorption	Langmuir	[58]
	Raw CNTs	3.19	1.29	Initial concentration= 5 mg/L, T=45^oC	Physi-sorption, Chemi-sorption	Langmuir	[58]
	Magnetic-functionalized MWCNTs	N/A	N/A	pH 6, Initial concentration =100 mg/ L	N/A	Experimental	[162]
	Oxidized CNTs sheets	92.59	75.84	pH 7, Initial concentration = 1200 mg/L, T = 298 K	Chemical interactions	Langmuir	[170]
	SWCNTs	24.07	N/A	pH 5, Initial concentration = 20 mg/L; contact time, 120 min, adsorbent dosage,	Physisorption	Langmuir	[171]

				50 mg/L, T = 298 ± 1 K			
	SWCNTs-COOH	55.89	N/A	pH 5, Initial concentration = 20 mg/L, contact time, 120 min, adsorbent dosage= 50 mg/L, T = 298 ± 1 K	Chemi-sorption	Langmuir	[171]
	Raw CNTs	1.661	0.657	pH 7, Initial concentration = 1 mg/L, CNT dosage = 50 mg	Electrostatic interactions	Langmuir	[177]
	HNO_3 oxidized CNTs	N/A	7.42	pH 8, Initial concentration =1 mg/L, Room Temperature	Electrostatic interactions	Experimental	[178]
	Pristine MWCNTs	0.05 mmol/g	N/A	pH 6.5-6.8, Initial concentration= 0.05-1.8mM	Electrostatic interactions	Langmuir	[179]
	O-MWCNTs	0.22 mmol/g	N/A	pH 6.5-6.8, Initial concentration= 0.05-1.8mM	Electrostatic interactions	Langmuir	[179]
	Alumina-decorated MWCNTs	27.21	0.948	pH 7, Initial concentration = 1 mg/L; adsorbent dosage= 50 mg/L	Electrostatic interactions, Physical adsorption, surface precipitation, surface complexation ,van der Waals interactions	Langmuir	[183]
As(III)	Multiwall carbon nanotube-zirconia nanohybrid (MWCNT-ZrO_2)	2000 µg/g	98.6 µg/g	pH 6, Initial concentration= 100 µg/ L	Chemi-sorption/ physisorption	Langmuir	[61]

	Fe-MCNTs	4	1.77	pH 8, Initial concentration = 1 mg/L	Electrostatic interactions	Langmuir	[114]
	Iron oxide coated multiwall carbon nanotubes	1723 µg /g	97.09 µg /g	pH 4, Initial concentration= 100 µg/ L	Electrostatic interactions/ complexation	Langmuir	[115]
As(V)	Multiwall carbon nanotube-zirconia nanohybrid (MWCNT-ZrO_2)	5000 µg/g	100.5 µg/g	pH 6, Initial concentration= 100 µg/ L	Chemi-sorption/ physisorption	Langmuir	[61]
	Iron oxide coated multiwall carbon nanotubes	189 µg /g	103.4 µg /g	pH 4, Initial concentration= 100 µg/ L	Electrostatic interactions/ complexation	Langmuir	[115]
	Fe(III) oxide coated ethylene-diamine modified MWCNTs	23.47	0.997	pH 4, Initial concentration= 100 µg/L	Ion exchange	Langmuir	[180]
Hg(II)	MWCNTs	13.16	0.493	Initial concentration= 1 mg/L	N/A	Langmuir	[112]
	MWCNTs	93.45	N/A	pH 6.5, Initial concentration= 50 mg/L, adsorbent dosage= 90 mg	N/A	Langmuir	[113]
	Nitrogen-doped magnetic CNTs	N/A	2.59 mmol/g	pH 8	Chemical adsorption	Langmuir	[116]
	Phenolic hydroxyl functional group P-	32.4	28.22	pH 4.3, Initial concentration =4 mg/L	Electrostatic interactions/ complexation	Langmuir	[181]

	MWCNT						
	OH-MWCNT	120.1	89.42	pH= 4.3, Initial concentration =4 mg/L	Electrostatic interactions/ complexation	Langmuir	[181]
	Carboxylic functional group COOH-MWCNT	127.6	81.57	pH= 4.3, Initial concentration =4 mg/L	Electrostatic interactions/ complexation	Langmuir	[181]
	Ox-MWCNTs	3.83	N/A	pH 7, Initial concentration= 100 µg/ L	Electrostatic interactions	Langmuir	[182]
	3-mercaptopropyltriethoxysilane (MPTS) grafted MWCNTs/ Fe_3O_4	65.52	63.65	pH 6.5, , Initial concentration= 50 mg/L, T= 25 ± 0.2 ^oC	Lewis acid–base interactions	Langmuir	[164]
	Ox-MWCNTs impregnated Chitosan beads	183.2	181.8	pH 4, Initial concentration= 1000 mg/L	Electrostatic interactions	Langmuir	[185]
	Sulphur containing MWCNTs (S-MWCNTs)	72.8 µg/g	N/A	pH 12.15, Initial concentration= 100 ppb	Chemi-sorption	Freundlich	[186]
	Amino and thiolated functionalized-MWCNTs	84.66	83.33	pH 6, Initial concentration =100 mg/L, CNTs dosage= 60 mg, T =25 ^oC, Time = 60 minutes	Physisorption	Langmuir	[187]
	Thiol derivatized single wall carbon nanotubes	131.58	74.2	pH 5, Initial concentration =40 mg/L, Time = 1 h, Adsorbent dose (m/v) = 0.25 mg/mL, T = 298	Chemi-sorption	Langmuir	[188]

				K			
	SWCNTs	40.16	N/A	pH 5, Time = 1 h, Adsorbent dose (m/v) = 0.25 mg/mL, T = 298 K	Electrostatic interactions	Langmuir	[188]
	MnO_2-coated carbon nanotubes	58.82	14.28	pH 5–7, Initial concentration =10 mg/L, contact time =80 min, T=50 ^oC	Electrostatic interactions	Langmuir	[189]
	MWCNTs	5.479	7.092	pH 6, Initial concertation=100-500 mg/L	Ion exchange	Langmuir	[190]
	Oxidized MWCNTs (MWCNT-OX)	27.32	27.77	pH 6, Initial concertation= 100-500 mg/L	Ion exchange	Langmuir	[190]
	Iodide incorporated MWCNT (CNT-I)	123.45	100	pH 6, Initial concertation= 100-500 mg/L	Ion exchange	Langmuir	[190]
	Functionalized (sulfur incorporated MWCNT (CNT-S)	151.51	100	pH 6, Initial concertation= 100-500 mg/L	Ion exchange	Langmuir	[190]
Cu(II)	HNO_3-modified CNTs	28.49	29	pH 5, Initial concentration = 10 mg/L, Room Temperature	Ion exchange	Langmuir	[52]
	CNTs	26.41	N/A	pH 5, Copper equilibrium concentration = 5 mg/L	Surface complexation / ion exchange	Langmuir	[109]
	CNTs/ calcium alginate composites	84.88	N/A	pH 5, Copper equilibrium concentration = 5 mg/L	Surface complexation / ion exchange	Langmuir	[109]

	Purified multi-walled carbon nanotubes (p-MWCNTs)	36.82	N/A	pH 5, initial concentration = 20 mg/L	Physical adsorption	D-R model	[110]
	Sulfonated multi-walled carbon nanotubes (s-MWCNTs)	43.16	N/A	pH 5, initial concentration = 20 mg/L	Electrostatic interactions	D-R model	[110]
	MWCNTs	3.19×10^{-5} mol/g	N/A	pH 5, Initial concentration = 2.36×10^{-4} mol/L, T = 303 K	Electrostatic interaction, surface complexation, surface precipitation	Langmuir	[111]
	MWCNTs impregnated with di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-n-octyl Phosphine oxide (TOPO)	N/A	4.90	pH 5, Initial concentration= 500 µg/L, adsorbent dosage= 500 mg	Electrostatic interaction	Experimental	[117]
	Magnetic-functionalized MWCNTs	N/A	N/A	pH 6, Initial concentration =100 mg/ L	N/A	Experimental	[162]
	Oxidized CNTs sheets	64.93	50.37	pH 7, Initial concentration = 1200 mg/L, T = 298 K	Chemical interactions	Langmuir	[170]
	Single walled carbon nanotubes (SWCNTs)	24.29	N/A	pH 5, Initial concentration = 20 mg/L; contact time, 120 min, adsorbent dosage, 50 mg/L, T = 298 ± 1 K	Physisorption	Langmuir	[171]

	SWCNTs-COOH	77	N/A	pH 5, Initial concentration = 20 mg/L; contact time, 120 min, adsorbent dosage, 50 mg/L, T = 298 ± 1 K	Chemi-sorption	Langmuir	[171]
	Oxidized MWCNTs	N/A	3.49	pH 9, Initial concentration = 1-20 mg/L, adsorbent dosage = 50 mg	Electrostatic interactions	Freundlich	[172]
	As-produced CNTs	8.25	N/A	pH 6, T= 300 K	Electrostatic interactions	Langmuir	[191]
	NaOCl-modified CNTs	47.39	N/A	pH 6, T= 300 K	Electrostatic interactions	Langmuir	[191]
	HNO_3-modified CNTs	13.87	N/A	pH 6, T= 300 K	Electrostatic interactions	Langmuir	[191]
	MWCNTs in the presence of humic acid (HA)	7.776 ± 0.538	N/A	Initial concentration = 20 mg/L, T= 293 K	Electrostatic interactions	Langmuir	[192]
	MWCNTs/ Fe_3O_4	38.91	19	pH 6, Concentration= 30 mg L	Electrostatic interactions	Langmuir	[193]
	Chitosan/poly (vinyl) alcohol thin adsorptive membranes modified amino functiona-lized CNTs	11.1	9.54	pH 5.5, Initial concentration= 30 mg/L, T= 20 ^oC	Ion exchange	Langmuir	[194]
	As-grown CNTs	14.4	N/A	pH 5.4, Cu^{2+} ion concentration= 20 mg/L	Precipitation	Langmuir	[195]
	Oxidized CNTs	27.6	N/A	pH 5.2, Cu^{2+} ion concentration=	Electrostatic interaction	Langmuir	[195]

				20 mg/L			
Zn (II)	Nitrogen-doped magnetic CNTs	N/A	9.31 mmol/g	pH 8	Chemical adsorption	Langmuir	[116]
	MWCNTs impregnated with di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-n-octyl phosphine oxide (TOPO)	N/A	4.82	pH 5, Initial concentration= 500 µg/L, adsorbent dosage= 500 mg	Electrostatic interaction	Experimental	[117]
	Oxidized CNTs sheets	74.63	58	pH 7, Initial concentration = 1200 mg/L, T = 298 K	Chemical interactions	Langmuir	[170]
	Pristine MWCNT	0.14 mmol/g	N/A	pH 6.5-6.8, Initial concentration= 0.08-3 mM	Electrostatic interactions	Langmuir	[179]
	O-MWCNT	0.27 mmol/g	N/A	pH 6.5-6.8, Initial concentration= 0.08-3 mM	Electrostatic interactions	Langmuir	[179]
	SWCNTs (NaOCl)	43.66	14.9	pH 7, S/L: 0.05/100, Initial concentration = 10 mg/L, T= 25 ^{o}C	Electrostatic interactions	Langmuir	[196]
	MWCNTs (NaOCl)	32.68	13.75	pH 7, S/L: 0.05/100, Initial concentration = 10 mg/L, T= 25 ^{o}C	Electrostatic interactions	Langmuir	[196]
	SWCNTs purified with sodium hypochlorite	46.94	16.18	Initial concentration= 60 mg/L, T = 45 ^{o}C	Electrostatic interactions	Langmuir	[197]

	MWCNTs purified with sodium hypochlorite	34.36	15.77	Initial concentration== 60 mg/L, T = 45 ^{o}C	Electrostatic interactions	Langmuir	[197]
	Multi-walled carbon nanotubes (MWCNTs) modified with chitosan	N/A	N/A	PH 7, Dosage = 200 mg, T= 298 K, Flow rate= 5 ml/min	Electrostatic interactions	N/A	[198]
	Function-alized carbon nanotubes	1.05	2.42	pH 10, Initial concentration = 1.1 mg/L, dosage = 0.09 g, agitation speed= 120 rpm, time =120 min	Electrostatic interactions	Langmuir	[199]
Ni (II)	MWCNTs	6.346×10^{-5} mol/g	2.9036	pH 5.4, m/V = 0.8 g/L, T= 293 K	Electrostatic interactions, π-π interaction	Langmuir	[41]
	Polyacrylic acid (PAA)-MWCNTs	6.615×10^{-6} mol/g	N/A	pH 5.4, m/V = 0.8 g/L, T= 293 K	Electrostatic interactions, π-π interaction	Langmuir	[41]
	HNO_3-treated MWCNTs	17.86	12.500	pH 6.5, Initial concentration = 20 mg/L, amount of adsorbent = 0.8 g/L, T= 338 K	Ion exchange	Langmuir	[42]
	MWCNTs/ Iron oxide	9.18	N/A	Initial concentration =6 mg/L, m/V =0.75 g/L	Ion exchange	Langmuir	[106]
	MWCNTs	18.083	N/A	pH 6, m/V =0.2 g/L	Electrostatic interaction	Langmuir	[108]
	Oxidized CNTs	49.261	N/A	pH 6, m/V =0.2 g/L	Electrostatic interaction	Langmuir	[108]
	Nitrogen-doped magnetic	N/A	8.06 mmol/g	pH 8	Chemical adsorption	Langmuir	[116]

	CNTs						
	MWCNTs impregnated with di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-n-octyl phosphine oxide (TOPO)	N/A	4.78	pH 5, Initial concentration= 500 µg/L, adsorbent dosage= 500 mg	Electrostatic interaction	Experimental	[117]
	Oxidized CNTs	9.80	8.75	pH 6.55 ±0.02, Initial concentration= 20 mg/L, T= 333 K	Electrostatic interaction	Langmuir	[126]
	HNO_3 oxidized CNTs	N/A	6.89	pH 8, Initial concentration =1 mg/L, Room Temperature	Electrostatic interactions	Experimental	[178]
	NaClO-modified MWCNTs	38.46	N/A	pH 7.0, Initial concentration= 10–80 mg/L, T=298 K	Electrostatic interaction	Langmuir	[200- 201]
	NaClO-modified SWCNTs	47.86	N/A	pH 7.0, Initial concentration= 10–80 mg/L, T=298 K	Electrostatic interaction	Langmuir	[200- 201]
Co (II)	MWCNTS/ Iron oxide	0.18 mmol/g	2.88	pH 6.4±0.1, Initial concentration = 4.2 mg/L, m/V = 0.5 g/L, T = 20±1 ^{o}C	Ion exchange, surface complexation	Langmuir	[118]
	Raw MWCNTs	3.40 x10^{-5} mol/g	N/A	pH = 6.8 ± 0.1, m/V = 1.0 g/L, Initial concentration = 1.69 x10^{-4} mol/L, T = 303.15 K	Surface complexation	Langmuir	[119]
	Poly(acrylic acid) grafted / MWCNTs	1.66x10^{-4} mol/g	N/A	pH = 6.8 ± 0.1, m/V = 1.0 g/L, Initial concentration = 1.69 x10^{-4} mol/L,	Surface complexation	Langmuir	[119]

				T = 343.15 K			
	Oxidized CNTs sheets	85.74	69.63	pH 7, Initial concentration = 1200 mg/L, T = 298 K	Chemical interactions	Langmuir	[170]
	Oxidized MWCNTs	N/A	2.60	pH 9, Initial concentration = 1-20 mg/L, adsorbent dosage = 50 mg	Electrostatic interactions	Freundlich	[172]
	MWCNTs–hydroxyl-apatite	3.55×10^{-4} mol/g	N/A	pH 6, T=293 K	Surface complexation	Langmuir	[184]

2.5 Surface Modification of CNTs

Surface modifications have proven to enhance the adsorption capacity and selectivity of CNTs towards the heavy metals. A number of surface modification techniques of CNTs have been reported in the literature such as acid treatment [3, 15, 17, 120, 129], impregnation with metal/metal oxides [53, 114-115, 163-164] and grafting the functional molecules/groups [105, 119, 168, 202-203]. Surface modifications of CNTs alter the properties of CNTs surface such as surface area, surface charge, hydrophobicity/ hydrophilicity and dispersion.

Acid modification can be achieved by chemical treatment of CNTs with various acids including HNO_3, $KMnO_4$, H_2O_2, H_2SO_4, NaOCl and HCl [3, 82, 120, 129]. Acid modification introduces different functional groups onto the CNTs surface that enhance the removal of heavy metals by different mechanisms, especially electrostatics interactions. Acid modifications also helped in removing impurities from the raw CNTs

surface and open the tips of the tubes. Characteristics of the modified CNTs are dependent on the properties of raw CNTs, method of modification and type of acid used [82]. Microwave-excited surface-wave plasma treatment also introduces oxygen-containing groups onto CNTs surface [204]. Fig. 2-5 represents schematic of the acid modification of CNTs, followed by divalent heavy metals adsorption on the surface of modified CNTs.

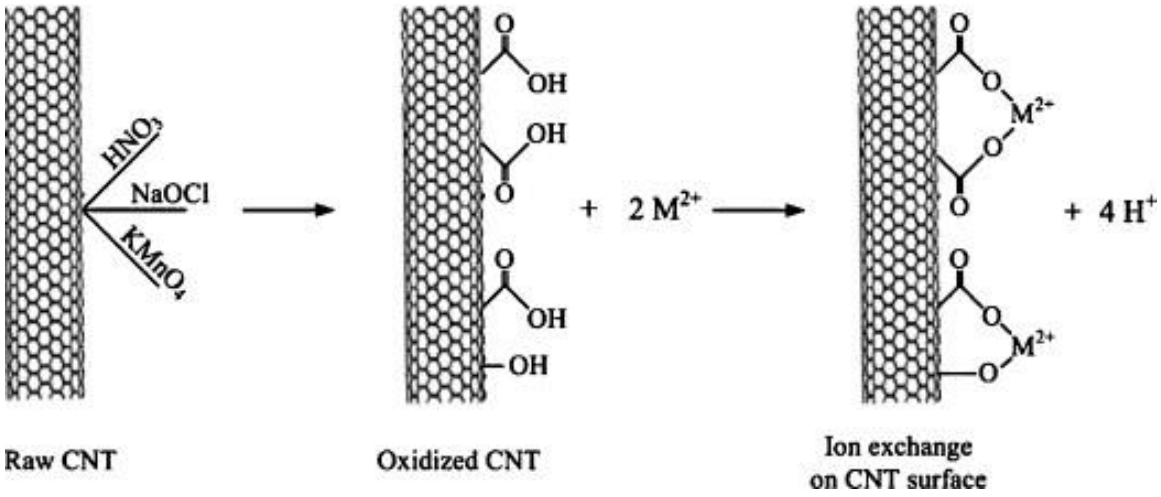


Figure 2-5: Schematic diagram of the major mechanism for sorption of divalent metal ions onto CNTs surface [82] (Reprint permission from Elsevier)

Grafting functional groups or molecules is another way to improve the surface characteristics of the CNTs. Numerous studies reported the removal of heavy metals from aqueous solution using the CNTs grafted with different functional groups [119,164, 168, 202-203]. A number of methods were employed in recent years to graft different function groups on the surface of CNTs including plasma technique, microwave and chemical modifications. However, plasma technique has the advantage of less energy requirement

and environment friendly process [119]. Fig. 2-6 shows schematic of typical grafting of CNTs surface and subsequent metal ions adsorption [107].

Modification of CNTs by metal oxide is a useful technique to improve the characteristics of the CNTs. CNTs modified with MnO_2 [163, 189], iron oxide [114-115, 193] and Al_2O_3 [53, 183] showed promising results for the removal of different heavy metals from aqueous solution. Fig. 7 shows schematic of modification of CNTs with alumina and possible interaction mechanisms of cadmium ions with the CNTs surface [183].

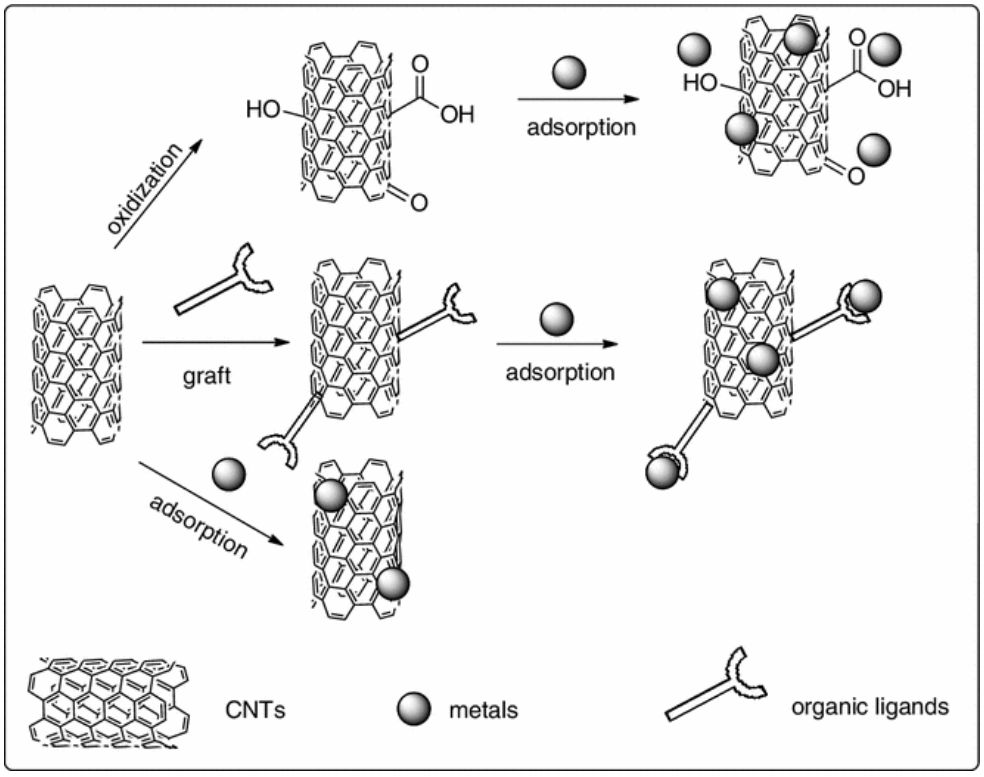


Figure 2-6: Schematic of grafting of CNTs and metals adsorption [107] (Reprint permission from Elsevier)

2.6 Sorption Mechanisms

Although the sorption mechanisms of metal ions onto CNTs are complex, however, the most dominant mechanisms reported in the literature are physical adsorption, chemical interaction, electrostatic attraction and sorption–precipitation [120, 129].

For CNTs with the surface functional groups, the chemical interaction between the CNTs and the metal ions is the most obvious mechanism [205]. Fig. 2-5 represents the attachment of divalent metal ions to the acid modified CNTs surface. Metal ions are sorbed on the CNTs surface and release the H^+ from the surface. This leads to decrease in solution pH. This process is strongly influenced by the initial metal ion concentration. With increase in initial concentration of metal ions, more ions are sorbed on the CNTs surface and the drop in pH value is increased. This is due to release of more H^+ ions from the surface site of CNTs into the solution.

Some researchers have found the take up of metal ions by the combined effect of electrostatic attraction and sorption–precipitation [52, 183]. Fig. 2-7 demonstrated the possible interaction mechanisms of cadmium ions adsorption on CNT/ Al_2O_3 surface. Cadmium ions are adsorbed on the surface of the modified CNTs via physical interactions, electrostatic interactions and van der Waals interactions occurring between the Cd(II) ions and hexagonally arrayed carbon atoms in the graphite sheet [183]. The role of solution pH is also critical in sorption of metal ions onto CNTs surface. At higher pH, more Zn^{2+} ions were adsorbed onto pure CNTs surface. This might be due to electrostatic interaction between the CNTs surface and divalent Zn^{2+} ions [196].

Generally, the raw CNTs have very low adsorption capacity for most of the heavy metals. However, the acid treatment of CNTs was observed to have significant effect on the

sorption capacity of CNTs. Oxidation of CNTs by $KMnO_4$, HNO_3 or NaClO was observed to increase the adsorption capacity of the CNTs. The oxygenous functional groups on the acid treated CNTs surface play a vital role in the adsorption of heavy metals. Various researchers have demonstrated that the acid modified CNTs have higher removal efficiency for heavy metals than raw CNTs [3, 15, 17, 120, 129]. Some researchers also showed that raw CNTs have higher adsorption for heavy metals than modified CNTs at certain concentration levels [104,206]. Beside acid modification, CNTs modified with other functional groups and metal oxides are also reported in literature.

The adsorption mechanism of different metal ions on CNTs is not the same and the affinity order of metals ions towards CNTs is different. Stafiej and Pyrzynska [172], reported that the affinity order of the certain metal ions towards CNTs is $Mn^{2+} < Zn^{2+} < Co^{2+} < Pb^{2+} < Cu^{2+}$ at pH 9. In two other studies, the following affinity orders were reported: $Pb^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+}$ [170] and $Cd^{2+} < Cu^{2+} < Zn^{2+} < Ni^{2+} < Pb^{2+}$ [82]. These results suggested that the adsorption of heavy metals on CNTs depends mainly on the properties of CNTs.

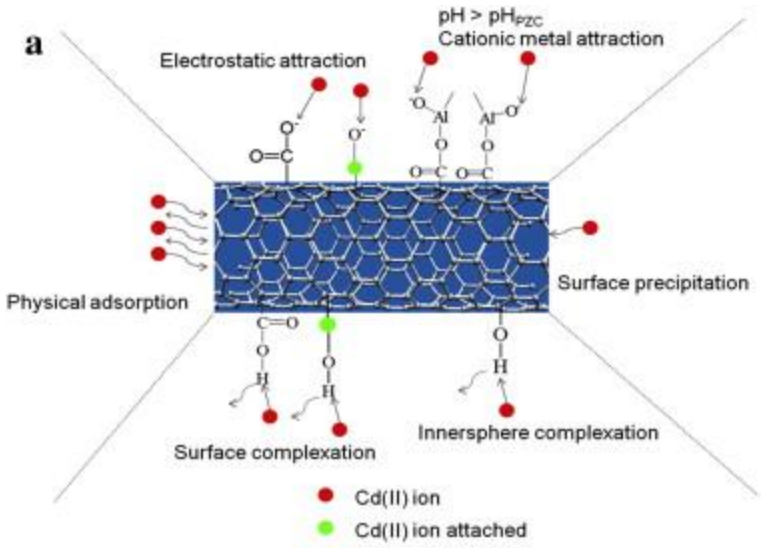


Figure 2-7: Schematic of the possible mechanism of cadmium ion adsorption on CNT/Al_2O_3 surface [183] (Reprint permission from Elsevier)

2.7 Factors Affecting the Adsorption of Heavy Metal Ions on CNTs

The main factors affecting adsorption of heavy metal ions on CNTs surface include the initial metal ion concentration, pH, contact time, CNT dosage, agitation speed, temperature, surface charge, ionic strength, isoelectric point and foreign ions.

2.7.1 Effect of pH

Solution pH plays a vital role in the adsorption of heavy metal ions onto the CNTs surface. At pH value higher than point of zero charge (pH_{PZC}), the adsorption of cations is higher due to electrostatic interactions between the cation ions and negative surface charge. On the other hand, the adsorption of cation ions is lower at low pH due to neutralization of surface charge. A change in pH also affects the competing complexation reactions and metal ion species. Hence, the adsorption capacity of CNTs is affected by change in pH of the solution [3-4, 82, 129]. The maximum removal of Cu^{2+}, Pb^{2+}, Cd^{2+},

Hg^{2+}, Co^{2+}, Zn^{2+} Cr^{6+} and Ni^{2+} by CNTs was observed at pH 5 [111], pH 5 [103], pH 7[177], pH 6.5 [113], pH 6.8 [119], pH 7 [196], pH 3 [15], pH 5.4 [41], respectively.

The species of heavy metal ions and properties of CNTs also have great influence on the adsorption of heavy metal ions onto CNTs. The pH_{PZC} of raw CNTs is in the range of pH 4–6 [172,205]. However, the acid treatment of CNTs was reported to have lower value of pH_{PZC} than those of raw CNTs [172,193,206-208]. Generally, the state of divalent metal ions in solution depends on the pH, however, the most common species include M^{2+}, $M(OH)^{+}$, $M(OH)_2^{0}$, $M(OH)^{3-}$ [41,126, 129, 208]. The release of H^+ ions by CNTs in solution can be shown by the reactions [129].

$$CNT–OH + H^{+} \leftrightarrow CNT–OH^{2+} \quad (1)$$

$$CNT–OH \leftrightarrow H+ + CNT–O^{-} \quad (2)$$

The adsorption mechanism of divalent metal ions onto CNTs is shown below.

$$CNT–OH^{2+} + M^{2+} \leftrightarrow [CNT–OHM^{2+}]^{2+} + H^{+} \quad (3)$$

$$CNT–O^{-} + M(OH)_n^{2-n} \leftrightarrow [CNT–O–M(OH)n^{2-n}]^{1-n} \quad (4)$$

At lower pH value (less than pH_{PZC}), M^{2+} is normally the dominant species in solution. Also the CNTs surface has a positive charge at pH value lower than pH_{PZC}. So the heavy metals ions are adsorbed on the surface due to competition between the M^{2+} and H^+ ions in the solution. However, at pH value higher than pH_{PZC}, the dominant divalent metal ions species in the solution is $M(OH)_n^{2-n}$. Also CNTs surface carry a negative charge at this pH value and the adoption is attributed to electrostatic interaction between the

divalent metal ions and CNTs surface. It is important to note that precipitation might take place at higher pH that also affects the removal of heavy metal ions [107].

Fig. 2-8 shows the distribution of lead species in the solution at different pH, while Fig. 2-9 shows the adsorption capacity (%) of lead ions at different pH. The adsorption of lead is low at pH < 6. This is due to the fact that the predominant lead specie is Pb^{2+} at this pH and there is a competition between H^+ and Pb^{2+} ions to occupy the limited adsorption site. However, in the range of pH 7–10, the dominant lead species in the solution are $Pb(OH)_2^0$ and $Pb(OH)^+$. Therefore it is believed that beside $Pb(OH)^+$ ions sorption on the surface, some precipitation of $Pb(OH)^0_2$ will also occur. Therefore, the removal is almost constant in this range due to the combined effect of these two opposing phenomena. At pH value above 10, the dominant species are $Pb(OH)^{3-}$ and $Pb(OH)^0_2$. The lower adsorption at this pH might be due to competition $Pb(OH)^{3-}$ and OH- ions and repulsion between the negative charge surface of CNTs and metal species at higher pH [209].

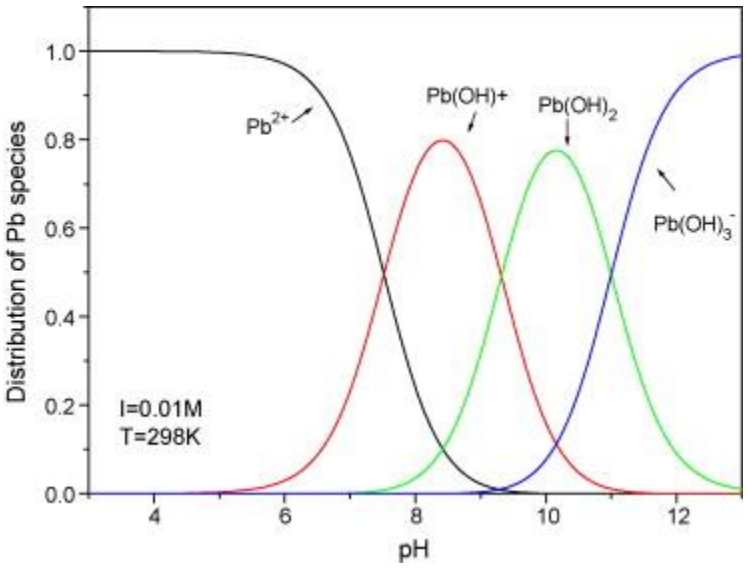


Figure 2-8: Distribution of Pb(II) species as a function of pH based on the equilibrium constants. [195] (Reprint permission from Elsevier)

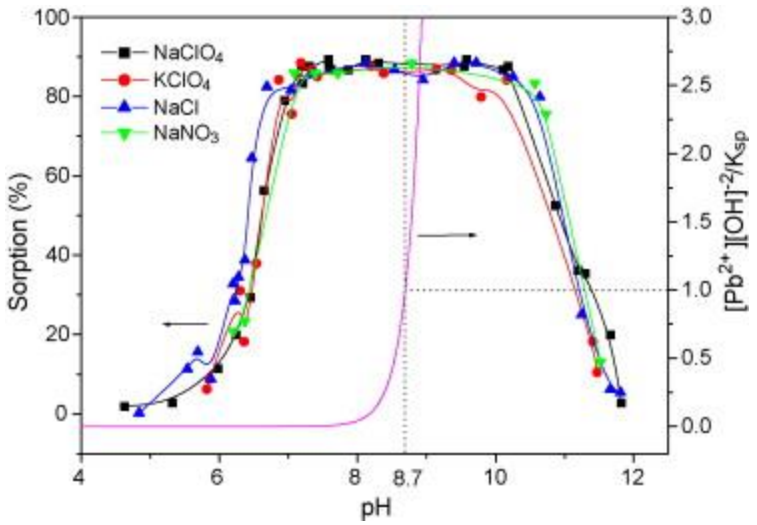
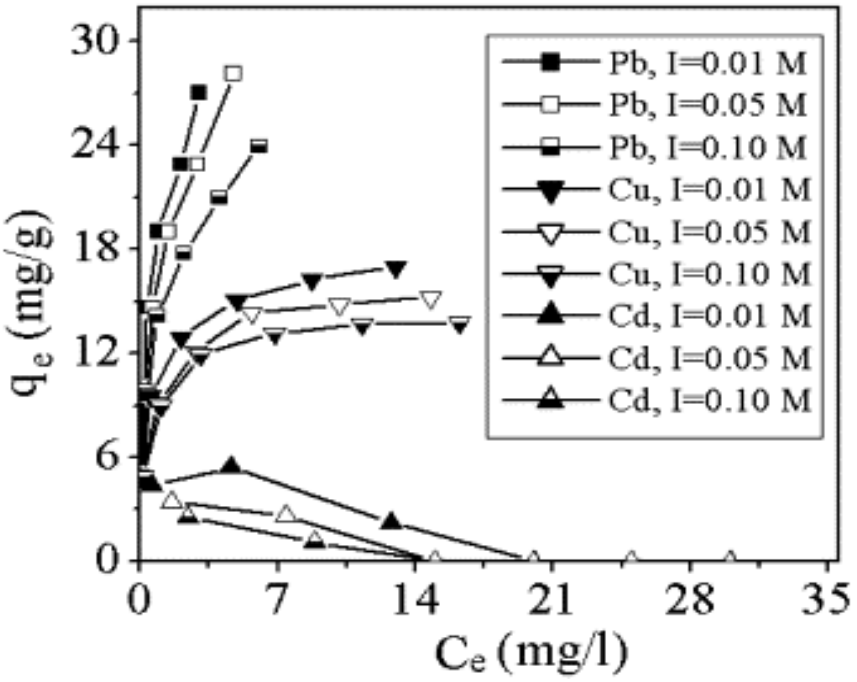


Figure 2-9: Distribution of Pb(II) species as a function of pH based on the equilibrium constants [195] (Reprint permission from Elsevier)

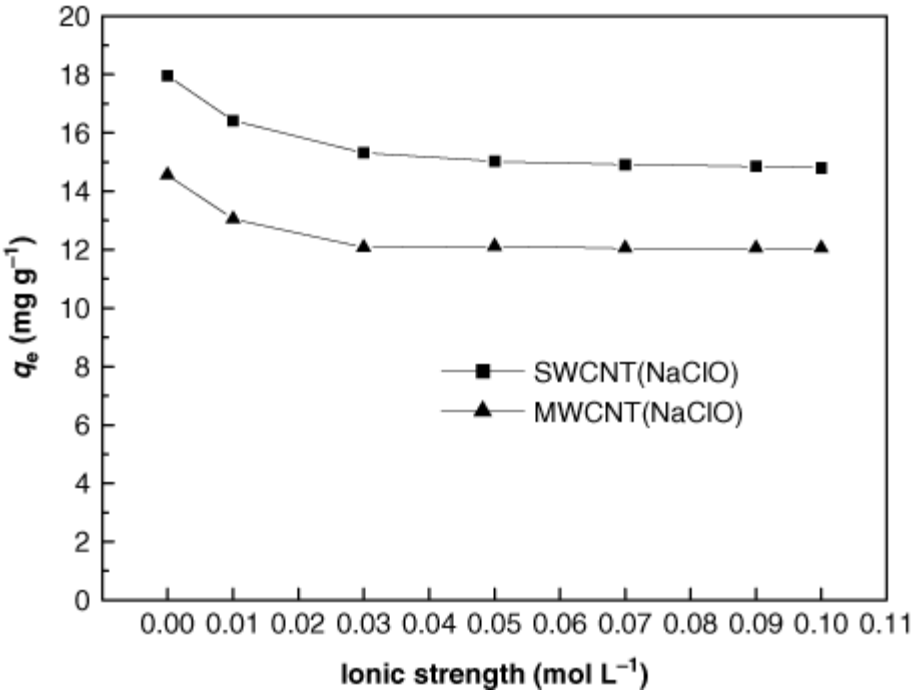
2.7.2 Effect of Ionic Strength

Ionic strength of heavy metal ions in the solution has influence on the adsorption of heavy metals onto CNTs surface. Generally, increasing the ionic strength has an adverse effect on the sorption of heavy metals. Fig. 2-10 shows the effect of ionic strength on the adsorption of heavy metal ions onto CNTs [52, 205].

The sorption of Ni^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} were observed to decrease with increase in ionic strength [52, 168, 171, 200]. This decrease in adsorption can be justified on the basis of two facts. Firstly, the ionic strength affects the activity coefficients of metal ions and hence the transfer of ions to CNTs surface is limited. Secondly, the formation of electrical double layer complexes between the cations and the CNTs limit the adsorption at high concentration of ions [52]. A similar behavior of decrease in Ni^{2+} sorption with increase in ionic strength of the solution is reported by Lu and Liu [205].



(a)



(b)

Figure 2-10: Effect of ionic strength on the competitive adsorption isotherms of (a) Pb^{2+}, Cu^{2+} and Cd^{2+} ions onto CNTs (b) Ni^{2+} sorption by oxidized CNTs [52, 205] (Reprint permission from Elsevier and John Wiley and Sons)

The adsorption of heavy metal ions is also affected by the competition of various metal ions to occupy the limited adsorption sites. At high metal ions concentration, the removal efficiency of CNTs is reduced. Competitive adsorption capacities of Cd^{2+}, Cu^{2+} and Pb^{2+} was observed to decrease with increase in metal ion concentration (Fig. 2-10). However, increase in pH and CNTs dosage has a positive effect on the adsorption capacity [52, 129].

2.7.3 Effect of CNTs Dosage

The dosage of CNTs also affects the adsorption of heavy metals. Increase in CNTs dosage can either increase or decrease the sorption of heavy metals. The sorption of Ni^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} is reported to increase with increase in the CNTs dosage [17, 52, 82,120]. This can be justified due to the availability of more sorption sites at higher CNTs dosage [82,120]. However, some studies reported a decrease in the sorption of Ni^{2+} and Co^{2+} with increase in CNTs dosage. Fig. 2-11 shows effect of the CNTs dosage on the percentage removal of Cd^{+2} ions. An increase in the Cd^{+2} ions removal was observed with increase in the adsorbent dosage for all types of CNTs [57]. This is due to the availability of more adsorption sites at higher CNTs dosage. It can also be observed that the acid modified CNTs have higher removal efficiency than raw CNTs. This might be due to improved electrostatic interaction between positive metal ions and negatively charged CNTs surface.

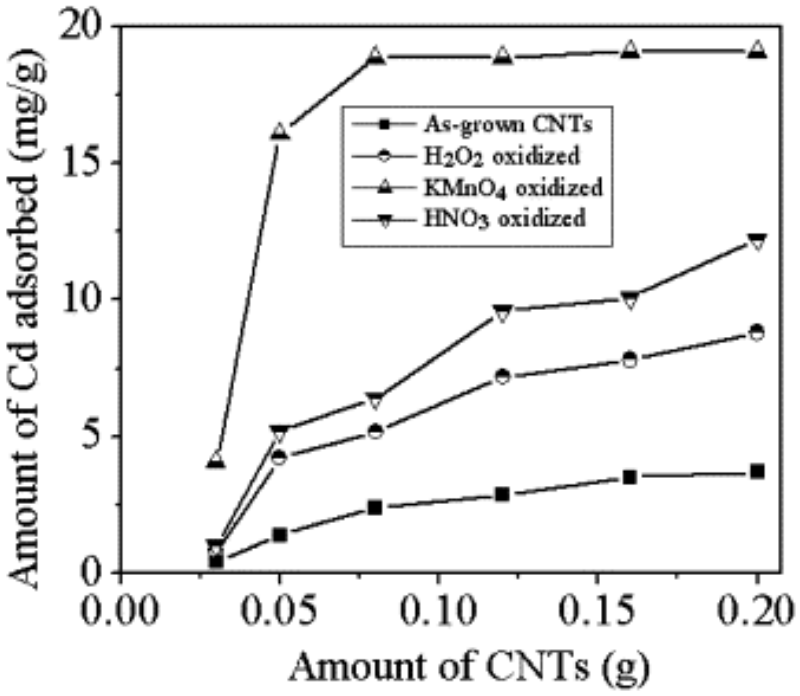


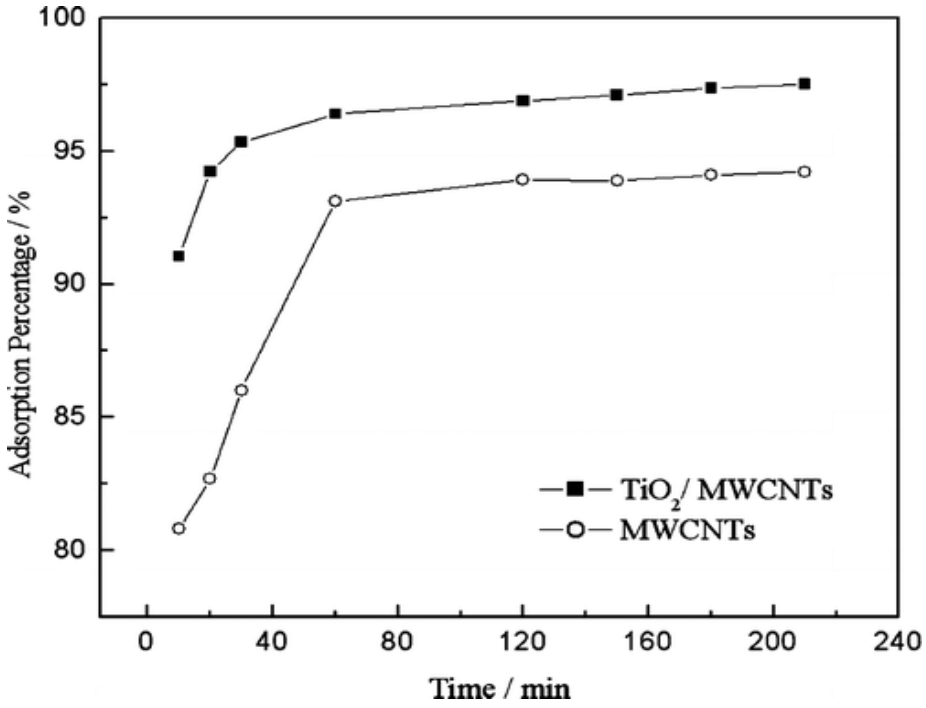
Figure 2-11: Effect of adsorbent dose on Cd (II) ion removal capacity [57] (Reprint permission from Elsevier)

2.7.4 Effect of Contact Time

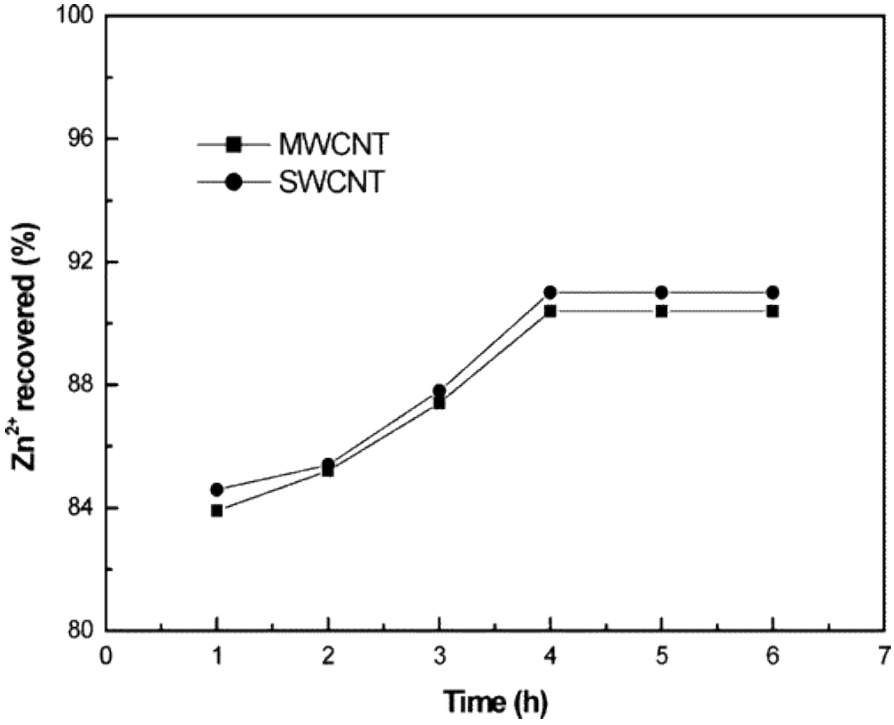
The contact time also has considerable effect on the adsorption of metal ions onto CNTs. Generally, with increase in contact time, the removal percentage of heavy metals increases until equilibrium is established. However, equilibrium is dependent strongly on the initial concentration of metal ions. Most of the studies confirmed that equilibrium established quickly, when the metal concentration is low. The sorption of Ni^{2+} takes 2 hours to reach equilibrium at initial concentration of 60 mg/L. However, with initial concentration of 10 mg/L, the equilibrium is established in one hour only [3, 82, 120].

Similarly, the equilibrium time required for Pb^{2+} sorption is 60, 50 and 20 min for the initial concentration of 30, 20 and 10 mg/L, respectively [48]. However, some studied suggested that adsorption is independent of metal ions concentrations. Fig. 2-12 shows

the effect of contact time on the adsorption of Pb^{2+} and Zn^{2+} ions by different types of MWCNTs [167,197].



(a)



(b)

Figure 2-12: Effect of time on the adsorption of (a) Pb(II) on MWCNTs and TiO_2/MWCNTs (b) Zn (II) on SWCNTs and MWCNTs [167, 197] Reprint permission from American Chemical Society)

2.7.5 Effect of Temperature

The effect of temperature on the sorption of heavy metal is reported in various studies. The most common observation is the increase in sorption capacity with rise in temperature. For example, sorption of Pb^{2+} and Zn^{2+} and is endothermic process and increases with rise in temperature [47-48,196]. This might be due to faster diffusion of metal ions through the solution due to decrease in solution viscosity at high temperature. Fig. 2-13 shows a similar temperature effect on the removal of Zn^{2+} by CNTs: (a) SWCNT and (b) MWCNT [197].

Activation energy of sorption (Ea) is also an index of the adsorption rate of heavy metals. The lower Ea value represents the higher sorption rate. The value of Ea also depends on the initial concentration of metal ions and type of CNTs. The value of Ea is higher at low initial concentration of metal ions. This might be due to low driving force for diffusion at low initial concentration. Also Ea value for MWCNTs is higher than SWCNTs due to more resistance to diffusion offered by multiple walls of MWCNTs [197].

2.7.6 Thermodynamic Parameters

The thermodynamic parameters reveal important information about the sorption of heavy metal ions onto the CNTs surface. The values of enthalpy ($\Delta H°$), entropy ($\Delta S°$) and Gibbs energy ($\Delta G°$) can be used to predict nature of the adsorption. Based on the calculated enthalpy values, the adsorption of Cd^{2+}, Cu^{2+} and Pb^{2+} ions was reported to physical process for SWCNTs and chemical process for SWCNTs-COOH , respectively [171]. The sorption of Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} by different types of CNTs is endothermic in nature, as suggested by the positive enthalpy value [48,127,171,197]. The positive entropy value indicated the increase in randomness at the solid/liquid interface.

This might be due to ion exchange process between the CNTs surface functional groups and heavy metal ions [127,197]. The sorption of Ni^{2+}, Zn^{2+} and Pb^{2+} is also believed to be spontaneous due to negative free energy value [48, 120].

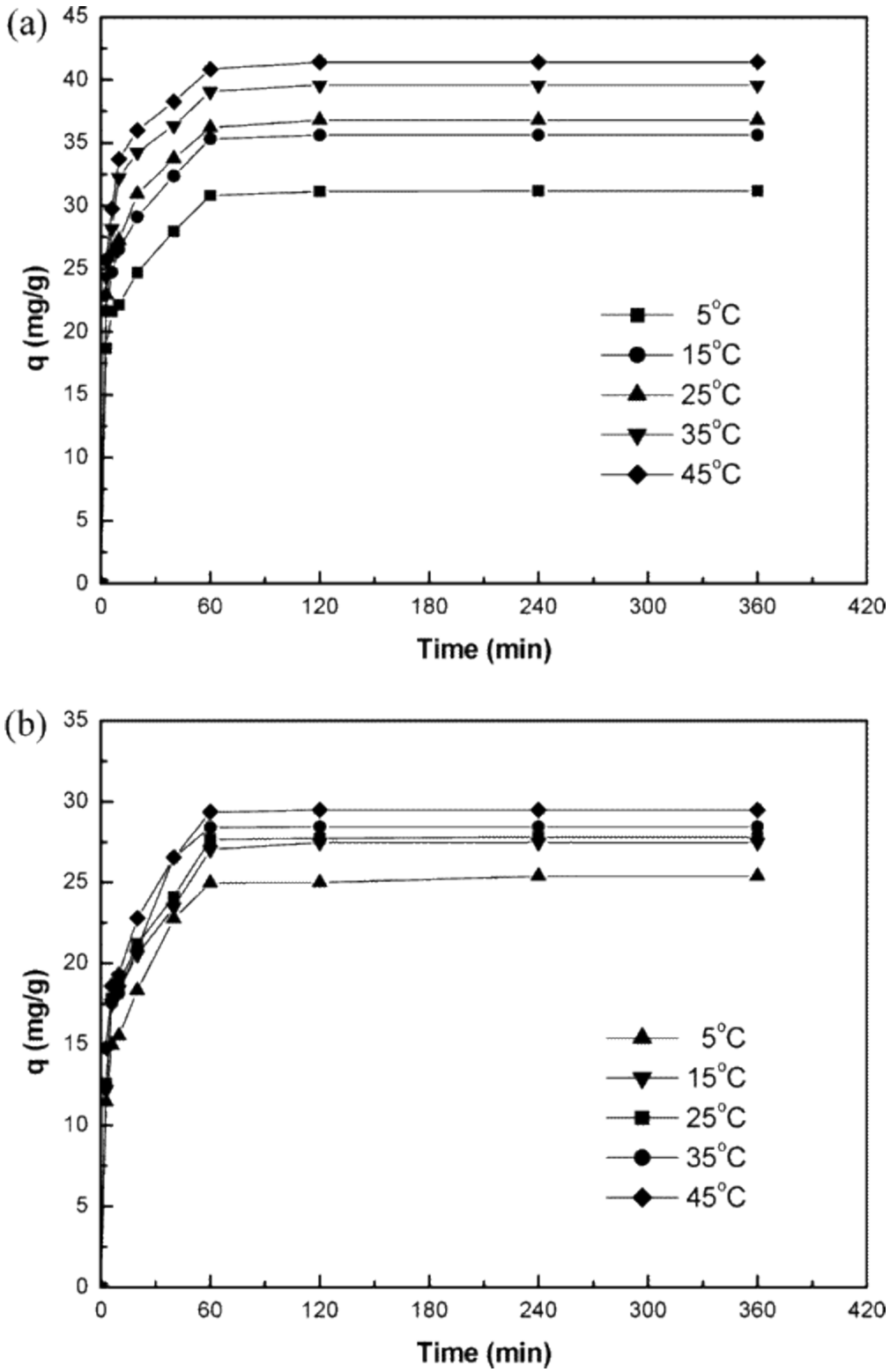
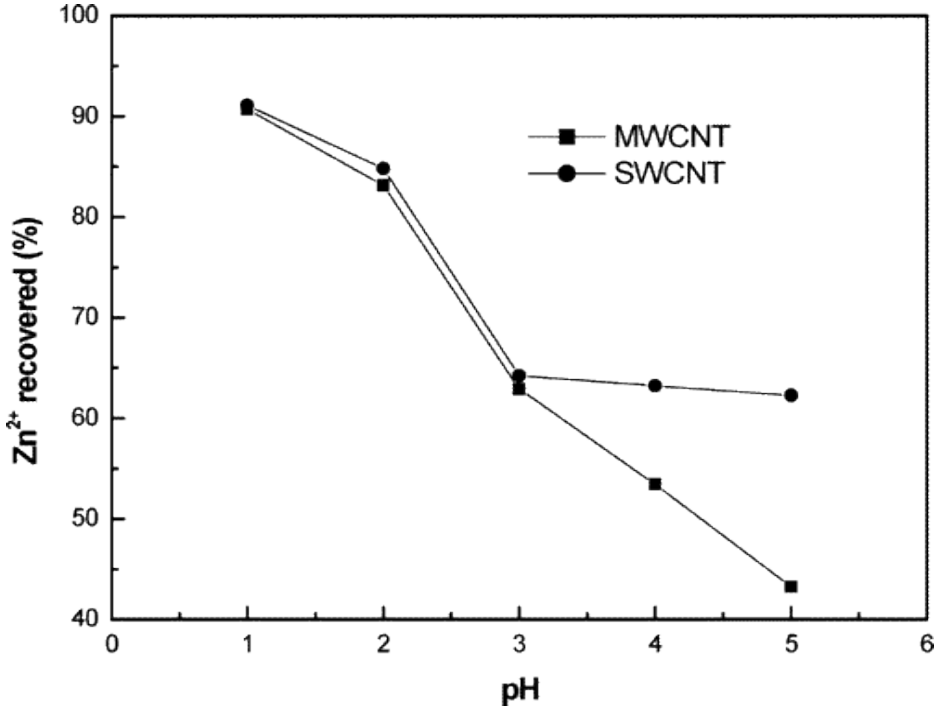


Figure 2-13: Effect of temperature on the sorption rate of Zn^{2+} by (a) SWCNT and (b) MWCNT [185] (Reprint permission from American Chemical Society)

2.8 Regeneration of CNTs

Regeneration of the adsorbent is not only necessary for the repeated use in practical applications but also highlight the economical aspect of the adsorbent. Regeneration of the CNTs is strongly dependent on the pH value of the regeneration solution. Studies have confirmed that CNTs can be regenerated by desorption of heavy metals ions from the CNTs surface. Regeneration of Zn^{2+} and Pb^{2+}at lower pH value is much higher than at higher pH [161, 197]. Beside pH, chemical treatment of the adsorbent may also desorb the deposited ions and regenerate the adsorbent. The MWCNTs were effectively regenerated by desorption of Ni^{2+}, Mn^{2+} and Cd^{2+} ions by treatment with HNO_3.

Fig. 2-14 shows the desorption of Zn^{2+} and Pb^{2+} from CNTs by adjusting the pH values of the solution [161,197]. It was observed that desorption of both the ions increases by decreasing the pH of the solution. The desorption of lead ions reaches from 0 to 100% quickly, when the pH was reduced from 5.4 to 2. The desorption value is very low at higher pH (>5), However, at lower pH (< 2.5), the desorption value is significantly increased [129, 161,197]. The results indicated that CNTs has potential to be reused in a number of treatment cycle and can make its place in cost effective adsorbent in future. More efforts are required to study the feasibility of the regeneration and reuse of CNTs [210].



(a)

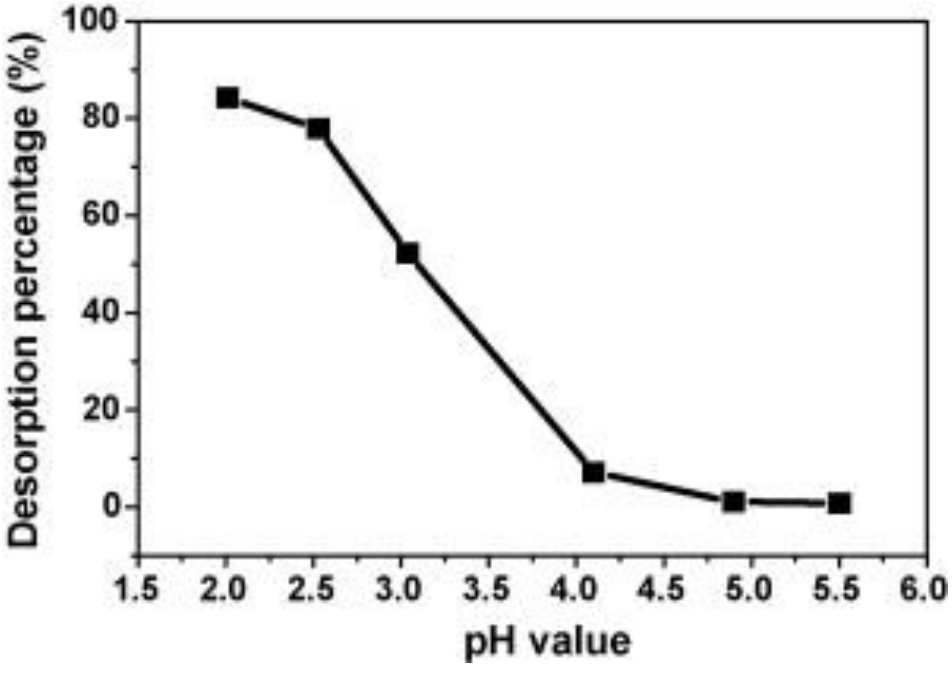


Figure 2-14: Desorption of (a) Zn^{2+} (b) Pb^{2+} from CNTs at different pH values of the solution [161,197] (Reprint permission from American Chemical Society and Elsevier)

2.9 Isotherm Equation

The adsorption data can be modeled using different equations including pseudo second order rate equation, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The sorption of metal ions onto CNTs is commonly correlated with the Langmuir or the Freundlich equations [48, 52, 61, 82, 111-115]. The Langmuir equation applicable to the sorption process on homogenous surfaces. However, the Freundlich equation is valid for sorption on the heterogeneous surface. Studies have shown that both the Langmuir and Freundlich equations represent the adsorption of different heavy metal ions onto CNTs [47,208]. In most cases, one model can best describe the adsorption process. Lead adsorption onto pure and modified CNTs can be best described by Langmuir equation [52, 61, 82, 111-115]. However, in some cases, the adsorption process can be well correlated by the Freundlich equation [48]. Some researchers employed other models to represent the adsorption of heavy metals onto CNTs. The adsorption of copper ions onto purified multi-walled carbon nanotubes (p-MWCNTs) and sulfonated multi-walled carbon nanotubes (s-MWCNTs) can best be described by D-R model [110].

2.10 Carbon Nanotube Toxicity

CNTs have emerged at the forefront of nanotechnology research and advancement. However, there has been a great concern on the potential environmental impacts of CNTs. Release of CNTs into the environment can lead to serious environmental problems. For instance, the nano sized carbon particles pose an occupational inhalation exposure hazard if entered in the working environment as suspended particulate matter (PM) [211]. Likewise, in water treatment plant, there is a risk that the CNTs might leach

after certain cycles and can harm the treatment plant. CNTs, not only, can disrupt the metabolic functions of microbes in the treatment plant but can also affect the aquatic life if enters to the environment [212]. CNTs have been observed to induce lung cellular proliferation and pulmonary inflammation in rats [211].

These biopersistence is a potential threat to the use of CNTs in water treatment plants. However, the toxicity of CNTs depends upon the type of CNTs, dimensions, presence of impurities, synthesis technique and physical state (i.e dispersed or agglomerated). In general, the agglomerated CNTs are more toxic as compared to well dispersed CNTs [213-214]. It is interesting to note that soluble CNTs did not have a toxic effect on cell viability [215]. Pristine CNTs can agglomerate easily and therefore, are more toxic than functionalized CNTs.

2.11 Current Challenges and Need for Further Research

In recent years, the potential of CNTs as an adsorbent in water treatment have been extensively explored. In spite of high costs, CNTs are expected to be a promising adsorbent in the future due to its high adsorption compared to many traditional adsorbents. A number of techniques are reported in the literature for the lab scale production of CNTs [216-217]. The researchers are now focusing on the large scale economical production of CNTs. Furthermore, many researchers are exploring novel techniques to modify the surface of CNTs to further improve their properties. Surface modification of CNTs has been observed to enhance the dispersion of CNTs in the solution, which is a serious issue with pure CNTs. The pure CNTs tend to aggregate in the aqueous solution due to van der Waal forces. This aggregation limits the available

adsorption sites for the pollutants to adsorb on the CNTs surface. Surface modification has a positive effect on the removal capacity of the CNTs. In some surface modification techniques, large amounts of chemicals are employed. This, again, lead to environmental pollution problems. Researchers are also in quest of novel environment friendly techniques for the surface modification of CNTs.

Plasma technique is one of the novel techniques to modify the surface of the CNTs with aim to improve the dispersion and adsorption capacity [218-220]. Separation of CNTs from the aqueous solution is challenging due to small size of nanotubes. Some techniques used to separate CNTs from the aqueous solutions are ultra-centrifugation separation and membrane filtration. However, these methods have the limitations of high energy requirement and membrane blockage, respectively. The magnetic separation seems to be best alternative method to overcome these limitations. Still, further efforts are required to make possible the practical applications of these materials in future.

CNTs have been proven to an excellent adsorbent for the removal of different heavy metals from wastewater. However, most of the applications of CNTs are on lab scale in batch experiments. Still, the feasibility of CNTs application in large scale treatment needs to be further studied [221]. Beside batch experiments, carbon nanotubes based membranes is an attractive way to utilize the unique properties of the CNTs for a number of applications including water treatment. CNTs have also been employed widely in the polymer membranes to improve their mechanical strength, antifouling characteristics and hydrophilicity [222]. These improved properties can ensure a more efficient way for the treatment of polluted water using these CNTs based membranes.

One of the main hurdles that limit the applications of CNTs in large scale operation is the cost of CNTs. Although researches are in quest of developing economical process for the mass production of CNTs, the current price does not suggest the applications of CNTs on large scale. Secondly, the potential hazardous effects of CNTs on the on human health and environment is also put questions to be answered. It is generally believed that the raw CNTs are more toxic as compared chemical functionalized CNTs. This may be due to presence of metal catalyst in raw CNTs [82]. It is expected that the due to increase in commercial production of CNTs, their price will be greatly reduced in future. Furthermore, development of the effective treatment techniques for the repeated availability and regeneration of CNTs can also reduce the cost of CNTs.

2.12 Conclusions

This review highlighted the removal of selected metal ions (Lead, chromium, cadmium, arsenic, copper, zinc and nickel) from water using CNTs. Different types of CNTs have been employed for the removal of heavy metals from water including raw, acid modified and functionalization with other materials. Although, raw CNTs has showed good adsorption potential for some of the metal ions, the modified CNTs showed the maximum adsorption capacity for most of the heavy metals. The different adsorption mechanism involves the physical adsorption, electrostatic interaction, surface complexation, chemical interaction between the surface functional groups and the metal ions. The effect of process parameters such as pH, CNTs dosage, time, ionic strength, temperature and surface charge on the adsorption of heavy metal ions on the CNTs surface was discussed. Feasibility of the reuse of CNTs through regeneration by desorption of metal ions was

also highlighted. This is an important factor in determining the potential use of CNTs in commercial treatment plants in future. However, further research work is essential to focus on feasible large scale production of CNTs and exploring the toxic effects of CNTs. The applications of CNTs in commercial water treatment plants are expected to be a breakthrough in future.

Acknowledgment

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References

[1] N.K. Srivastava, C.B. Majumder, Novel biofiltration methods for the treatment of heavy metals from industrial wastewater, J. Hazard. Mater. 151 (2008) 1-8.

[2] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arabian J. Chem. 4 (2011) 361–377.

[3] F. Fu, Q.Wang, Removal of heavy metal ions from wastewaters: A review. J. Environ. Manage. 92 (2011) 407-418.

[4] P.A.S.S. Marques, M.F. Rosa, H.M. Pinheiro, pH effects on the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solution by waste brewery waste, Bioprocess Eng. 23 (2000) 135-141.

[5] X. Qu, P.J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res. 47 (12) (2013) 3931–3946.

[6] G. F. Nordberg, B. Flower, M. Nordberg, L. Friberg, Handbook on the Toxicology of Metals, 3rd ed. Academic Press (2007).

[7] M. M. Rao, A. Ramesh, G.P.C. Rao, K. Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from ceiba pentandra hulls, J. Hazard. Mater. B 129 (2006)123–129.

[8] U.S. Environmental Agency, Drinking Water Contaminants, Available from: http://www.epa.gov/safewater/contaminants/index.html, May 17, 2015.

[9] World Health Organization International Standards for Drinking Water, WHO, Geneva, 2008.

[10] D. Mohana, C.U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. B137(2006) 762–811.

[11] M. A. Atieh, O.Y. Bakather, B.S. Tawabini, A.A. Bukhari, M. Khaled, M. Alharthi, M. Fettouhi, F. A. Abuilaiwi, Removal of chromium (III) from water by using modified and nonmodified carbon nanotubes, J Nanomater. (2010) 232378. doi.org/10.1155/2010/232378.

[12] J. Fang, Z.M. Gu, Cr(VI) removal from aqueous solution by activated carbon coated with quaternized poly(4-vinylpyridine), Environ. Sci. Technol. 41(2007) 4748–4753.

[13] D. Mohan, K.P. Singh, V. K. Singh, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, J. Hazard. Mater. 135 (2006) 280–295.

[14] J. Hu, C. Chen, X. Zhu, X.Wang, Removal of chromium from aqueous solution by using oxidized multiwalled carbon nanotubes, J. Hazard. Mater. 162 (2009) 1542–1550.

[15] Ihsanullah, F. A. A. Khaldi, B. A. Sharkh, A. M. Abulkibash, M. I. Qureshi, T. Laoui, M. A. Atieh, Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes, Desalin. Water Treat. (2015). doi: 10.1080/19443994.2015.1021847.

[16] S. S. Liu, Y.Z. Chen, L.D. Zhang, G.M. Hua, W. Xu, N. Li, Y. Zhang, Enhanced removal of trace Cr(VI) ions from aqueous solution by titanium oxide–Ag composite adsorbents, J. Hazard. Mater. 190 (2011) 723-728.

[17] Ihsanullah, F. A. A. Khaldi, B. Abusharkh, M. Khaled, M. A. Atieh, M.S. Nasser, T. Laoui, S. Agarwal, I. Tyagi, V. K. Gupta, Adsorptive removal of Cadmium (II) ions from liquid phase using acid modified carbon-based adsorbents, J. Mol. Liq. 204 (2015) 255-263.

[18] M. Arias, M.T. Barral, J.C. Mejuto, Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids, Chemosphere 48 (2002) 1081–1088.

[19] Q. Li, S. Wu, G. Liu, X. Liao, X. Deng, D. Sun, Y. Hu, Y. Huang, Simultaneous biosorption of cadmium (II) and lead (II) ions by pretreated biomass of Phanerochaete chrysosporium, Sep. Purif. Technol. 34 (2004) 135–142.

[20] C. F. Harvey, C. H. Swartz, A. B. Badruzzaman, N. K. Blute, W. Yu, M.A. Ali, J. Jay, R. Beckie, V. Niedan, D. Brabander, P.M. Oates, K.N. Ashfaque, S. Islam, H. F. Hemond, M.F. Ahmed. Arsenic Mobility and Groundwater Extraction in Bangladesh, Science 298 (2002) 1602-1606.

[21] J.F. Ferguson, J. Gavis, Review of the arsenic cycle in natural waters. Water Res. 6 (1972) 1259–1274.

[22] R. R. Lauwerys, J.P. Buchet, H. Roels, The determination of trace levels of arsenic in human biological materials, Arch. Toxicol. 41 (1979) 239-247.

[23] I. Villaescusa, I.C. Bollinger, Arsenic in drinking water: sources, occurrence and health effects (a review), Rev. Environ. Sci Biotechnol. 7 (2008) 307–323.

[24] V.K. Sharma, M. Sohn, Aquatic arsenic: Toxicity, speciation, transformations, and remediation, Environ. Int. 35 (2009) 743–759.

[25] W. P. Inskeep, T.R. McDermott, S.E. Fendorf, Arsenic (V/III) cycling in soils and natural waters: Chemical and microbiological processes. In W. T. Frankenberger, Jr. (Ed.) Environmental Chemistry of Arsenic. p. 183. Marcel Dekker, Inc., New York. ISBN 0824706765(2002).

[26] J.C. Ng, Environmental contamination of arsenic and its toxicological impact on humans, Environ. Chem. 2 (2005)146–160.

[27] S. E. Fendorf, J. E. Matthew, P. Grossel, D.L. Sparks, Arsenate and chromate retention mechanism on goethite, Surface structure, Environ. Sci. Technol. 3 (1997) 315–320.

[28] Subcommittee on Arsenic in Drinking Water, National Research Council Arsenic in Drinking Water, The National Academies Press (1999) 177-192.

[29] W. Goessler, D. Kuehnelt, Analytical methods for the determination of arsenic and arsenic compounds in the environment. In W. T. Frankenberger, Jr. (Ed.) ―Environmental Chemistry of Arsenic. p. 27. Marcel Dekker, Inc., New York. ISBN 0824706765 (2002).

[30] A.H. Smith, C.H. Rich, M.N. Bates, H.M. Goeden, I.H. Picciotto, H.M. Duggan, R. Wood, M.J. Kosnett, M.T. Smith, Cancer risks from arsenic in drinking water. Environ. Health Perspect. 97 (1992) 259–267.

[31] H.G. Fuhrman, J.C. Tjell, D. McConchie, Arsenic removal from water using seawater-neutralized red mud, Environ. Sci. Technol. 38(8) (2004) 2428-2434.

[32] J.C.J. Bonzongo, K.J. Heim, Y. Chen, W.B. Lyons, J.J. Warwick, G.C. Miller, P.J. Lechler, Mercury pathways in the Carson River-Lahontan Reservoir System, Nevada, USA, Environ. Toxicol. Chem. 15 (1996) 677-683.

[33] W. Takaaki, S. Katsuyasu, Adsorption behaviors of mercury from aqueous solution using sulfur-impregnated adsorbent developed from coal, Fuel Process. Technol. 92(2011) 71322–1327.

[34] M. R. Awual, M. Ismael, T. Yaita, S. A. E. Safty, H. Shiwaku, Y. Okamoto, S. Suzuki. Trace copper (II) ions detection and removal from water using novel ligand modified composite adsorbent, Chem. Eng. J. 222 (2013) 67-76.

[35] B.A.M. Al-Rashdi, D.J. Johnson, N. Hilal, Removal of heavy metal ions by nanofiltration, Desalination 315 (2013) 2–17.

[36] C. Liu, R. Bai, Q.S. Ly, Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: behaviors and mechanisms, Water Res. 42 (2008) 1511–1522.

[37] J. Peric, M. Trgo, N.V. Medvidovic, Removal of zinc, copper and lead by natural zeolite-a comparison of adsorption isotherms, Water Res. 38 (2004) 1893–1899.

[38] J. Bertinato, M.R. L'Abbe, Maintaining copper homeostasis: regulation of copper-trafficking proteins in response to copper deficiency or overload, J. Nutr. Biochem. 15 (2004) 316–322.

[39] Y.H. Chan, J. Chen, Q. Liu, S.E. Wark, D.H. Son, J.D. Batteas, Ultrasensitive copper(II) detection using plasmon-enhanced and photo-brightened luminescence of CdSe quantum dots, Anal. Chem. 82 (2010) 3671–3678.

[40] E.A. Deliyanni, E.N. Peleka, K.A. Matis, Removal of zinc ion from water by sorption onto iron-based nanoadsorbent, J. Hazard. Mater. 141 (2007) 176–184.

[41] S.T. Yang, J.X. Li, D.D. Shao, J. Hu, X.K. Wang, Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA, J. Hazard. Mater. 166 (2009) 109–116.

[42] I. Mobasherpour, E. Salahi, M. Ebrahimi, Removal of divalent nickel cations from aqueous solution by multi-walled carbon nano tubes: equilibrium and kinetic processes, Res. Chem. Intermed. 38(2012) 2205-2222.

[43] Q.Y. Chen, Z. Luo, C. Hills, G. Xue, M. Tyrer, Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon dioxide, Water Res., 43 (2009) 2605–2614.

[44] V.J. Inglezakis, M.A. Stylianou, D. Gkantzou, M.D. Loizidou, Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents, Desalination, 210 (2007) 248–256.

[45] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, Bioresour. Technol. 99 (2008) 3935–3948.

[46] R. Sabry, A. Hafez, MaalyKhedr, A. E. Hassanin, Removal of lead by an emulsion liquid membrane Part I, Desalination 212 (2007) 165–175.

[47] Y.H. Li, S.G. Wang, J.Q. Wei, X.F. Zhang, C.L. Xu, Z.K. Luan, D.H. Wu, B.Q. Wei, Lead adsorption on Carbon Nanotubes, Chem. Phys. Lett. 357 (2002) 263–266.

[48] Y.H. Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu, Adsorption thermodynamics, kinetic and desorption studies of Pb^{2+} on carbon nanotubes, Water Res. 39 (2005) 605-609.

[49] Y.H. Li, Y. Zhu, Y. Zhao, D. Wu, Z. Luan, Different morphologies of carbon nanotubes effect on the lead removal from aqueous solution, Dia. Rel. Mat. 15(2006) 90-94.

[50] L. Lv, K. Wang, X.S. Zhao, Effect of operation conditions on the removal of Pb^{2+} by microporous titanosilicate ETS-10 in a fixed bed column, J. Coll. Interf. Sci. 305(2007) 218-225.

[51] C. Liu, P.M. Huang, Kinetics of lead adsorption by iron oxides formed under the influence of citrate, Geochim. Cosmochimi. Acta. 67(2003) 1045–1054.

[52] Y.H. Li, J. Ding, Z. Luan, Z.Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes, Carbon 41(2003) 2787-2792.

[53] V.K. Gupta, S. Agarwal, T.A. Saleh, Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal, J. Hazard. Mater. 185(2011) 17-23.

[54] A. Salem, R. A. Sene, Removal of lead from solution by combination of natural zeolite–kaolin–bentonite as a new low-cost adsorbent, Chem. Eng. J. 174(2011) 619-628.

[55] L. Hajiaghababaei, A. Badiei, M.R. Ganjali, S. Heydari, Y. Khaniani, G.M. Ziarani, Highly efficient removal and preconcentration of lead and cadmium cations from water and wastewater samples using ethylenediamine functionalized SBA-15, Desalination 266 (2011) 182-187.

[56] Y. Li, Z. Jin, Z. Li, A novel and simple method to synthesize SiO_2-coated Fe nanocomposites with enhanced Cr(VI) removal under various experimental conditions, Desalination 288(2012) 118-125.

[57] Y. H.Li, S. Wang, Z.Luan, J.Ding, C.Xu, D. Wu, Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes, Carbon 41 (2003) 1057–1062.

[58] G. D. Vukovic, A. D. Marinkovic, M. Colic, M. D Ristic, R. Aleksic, A. A. P.Grujic, P S. Uskokovic, Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes, Chem. Eng. J. 157(2010) 238–248.

[59] D. Mohan, C.U.P. Jr, Arsenic removal from water/wastewater using adsorbents - A critical review, J. Hazard. Mater. 142(2007) 1–53.

[60] R. Chen, C. Zhi, H. Yang, Y. Bando, Z. Zhang, N. Sugiur, D. Golberg, Arsenic (V) adsorption on Fe_3O_4 nanoparticle-coated boron nitride nanotubes, J. Colloid Interface Sci. 359 (2011) 261–268.

[61] S.A. Ntim, S. Mitra, Adsorption of arsenic on multiwall carbon nanotube–zirconia nanohybrid for potential drinking water purification, J. Colloid Interface Sci. 375(2012) 154–159.

[62] M.B. Baskan, A. Pala, Removal of arsenic from drinking water using modified natural zeolite, Desalination 281(2012) 396–403.

[63] G.A. Gill, K.W. Bruland, Mercury speciation in surface freshwater systems in California and other areas, Environ. Sci. Technol. 24(1990) 1392-1400.

[64] N.F. Di, A. Erto, A. Lancia, D. Musmarra, Mercury adsorption on granular activated carbon in aqueous solutions containing nitrates and chlorides, J. Hazard. Mater. 192 (2011) 1842-1850.

[65] G. Meenakshi, B. Mamta, D. Rashmi, Removal of mercury from water by fixed bed activated carbon columns, J. Hazard. Mater. 171 (2009) 1009-1015.

[66] S. Hadi, K. Tahereh, Investigation of nitric acid treatment of activated carbon for enhanced aqueous mercury removal, J. Ind. Eng. Chem. 16 (2010) 852-858.

[67] J. Khosravi, A. Alamdari, Copper removal from oil-field brine by coprecipitation, J. Hazard. Mater. 166 (2009) 695–700.

[68] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 45 (2003) 219–243.

[69] S. Rio, C. F. Brasquet, L.L. Coq, P. Courcoux, P.L. Cloirec, Experimental design methodology for the preparation of carbonaceous sorbents from sewage sludge by chemical activation-application to air and water treatments, Chemosphere 58 (2005) 423–437.

[70] M.S. Rahman, M.R. Islam. Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust, Chem. Eng. J. 149 (2009) 273–280.

[71] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[72] B. Al-Rashdi, C. Somerfield, N. Hilal, Heavy metals removal using adsorption and nanofiltration techniques, Sep. Purif. Rev. 40 (2011) 209–259.

[73] H. Hasar, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, J. Hazard. Mater. 97 (2003) 49–57.

[74] A.H. Hawari, C.N. Mulligan, Biosorption of lead (II), cadmium (II), copper (II) and nickel (II) by anaerobic granular biomass, Bioresour. Technol. 97(2006) 692-700.

[75] K.C. Justi, V.T. Favere, M.C. Laranjeira, A. Neves, R.A. Peralta, Kinetics and equilibrium adsorption of Cu(II), Cd(II), and Ni(II) ions by chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formylphenol, J. Colloid Interface Sci. 291(2005) 369-374.

[76] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, S. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, Adv. Environ. Res. 4(2000) 19-29.

[77] K. Kadirvelu, C.F. Brasquet, P.L. Cloirec, Removal of Cu(II), Pb(II), and Ni(II) by adsorption onto activated carbon cloths, Langmuir 16 (2000) 8404-8409.

[78] Z. Reddad, C. Gerente, Y. Andresp, P.L. Ecloirec, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol. 36(2002) 2067-2073.

[79] O. Yavuz, Y. Altunkaynak, F. Gu¨zel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Res. 37(2003) 948-952.

[80] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, Sep. Purif. Technol. 50 (2006) 132–140.

[81] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash, Waste Manage. 22 (2002) 821–830.

[82] G.P. Rao, C. Lu, F. Su, Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review, Sep. Purif. Technol. 58 (2007) 224–231.

[83] M. Sekar, V. Sakthi, S. Rengaraj, Kinetics equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell, J. Colloid Interface Sci. 279 (2004) 307–313.

[84] H.K. An, B.Y. Park, D.S. Kim, Crab shell for the removal of heavy metals from aqueous solution, Water Res. 35(2011) 3551-3556.

[85] J. Ayala, F. Blanco, P. Garcia, P. Rodriguez, J. Sancho, Asturian fly ash as a heavy metals removal material, Fuel 77 (1998) 1147–1154.

[86] C.H. Weng, C.P. Huang, Adsorption characteristics of Zn(II) from dilute aqueous solution by fly ash, Colloid. Surf. A 247 (2004) 137–143.

[87] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat, Wat. Res. 33 (1999) 578–584.

[88] S.C. Pan, C.C. Lin, D. Hwa, Reusing sewage sludge ash as adsorbent for copper removal from wastewater, Resour. Conserv. Recycl. 39 (2003) 79–90.

[89] B. Biskup, B. Subotic, Removal of heavy metal ions from solutions using zeolites. III. Influence of sodium ion concentration in the liquid phase on the kinetics of exchange processes between cadmium ions from solution and sodium ions from zeolite A, Sep. Sci. Technol. 39 (2004) 925–940.

[90] F. Ekmekyapar, A. Aslan, Y.K. Bayhan, A. Cakici, Biosorption of copper (II) by nonliving lichen biomass of cladonia rangiformis hoffm, J. Hazard. Mater. 137 (2006) 293–298.

[91] W. Chu, Lead metal removal by recycled alum sludge, Water Res. 33 (1999) 3019–3025.

[92] E.J. Kim, C.S. Lee, Y.Y. Chang, Y.S. Chang, Hierarchically structured manganese oxide-coated magnetic nanocomposites for the efficient removal of heavy metal ions from aqueous systems, ACS Appl. Mater. Inter. 5(19) (2013) 9628-9634.

[93] C.V. Diniz, F.M. Doyle, V.S.T. Ciminelli, Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solutions by the chelating resin dowex M-4195, Sep. Sci. Technol. 37 (2002) 3169–3185.

[94] S.Y. Kang, J.U. Lee, S.H. Moon, K.W. Kim, Competitive adsorption characteristics of Co^{2+}, Ni^{+2}, and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater, Chemosphere 56(2004) 141-147.

[95] A. Aklil, M. Mouflihb, S. Sebti, Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent, J. Hazard. Mater. A112(2004) 183–190.

[96] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Physicochemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118(2006) 83–98.

[97] T. Mohammadi, A. Mohebb, M. Sadrzadeh, A. Razmi, Modeling of metal ion removal from wastewater by electrodialysis, Sep. Purif. Technol. 41(2005) 73–82.

[98] P. Kajitvichyanukula, J. Ananpattarachaia, S. Pongpom, Sol–gel preparation and properties study of TiO_2 thin film for photocatalytic reduction of chromium(VI) in photocatalysis process, Sci. Technol. Adv. Mater. 6(2005) 352–358.

[99] Q. Chang, G. Wang, Study on the macromolecular coagulant PEX which traps heavy metals, Chem. Eng. Sci. 62(2007) 4636-4643.

[100] J. Rubio, M.L. Souza, R.W. Smith, Overview of flotation as a wastewater treatment technique, Miner. Eng. 15(2002) 139-155.

[101] Z.C. Di, Y.H. Li, Z.K. Luan, J. Liang, Adsorption of chromium(VI) ions from water by carbon nanotubes, Adsorpt. Sci. Technol. 22(2004) 467–474.

[102] H. Gu, S.B. Rapole, Y. Huang, D. Cao, Z. Luo, S. Wei, Z. Guo, Synergistic interactions between multi-walled carbon nanotubes and toxic hexavalent chromium, J. Mater. Chem. A 1 (2013) 2011–2021.

[103] N.A. Kabbashi, M.A. Atieh, A.A. Mamun, M.E.S Mirghami, M.D.Z. Alam, N. Yahya, Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution, J. Environ. Sci. 21(2009) 539-544.

[104] H.J. Wang, A.L. Zhou, F. Peng, H. Yu, J. Yang, Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb(II), J. Colloid Interface Sci. 316 (2007) 277-283.

[105] D. Shao, J. Hu, X. Wang, Plasma induced grafting multiwalled carbon nanotube with chitosan and its application for removal of UO_2^{2+}, Cu^{2+}, and Pb^{2+} from aqueous solutions, Plasma Processes Polym. 7(2010) 977-985.

[106] C.L. Chen, J. Hu, D.D. Shao, J.X. Li, X.K. Wang, Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II), J. Hazard. Mater. 164(2009) 923–928.

[107] J.G. Yu, X.H. Zhao, L.Y. Yu, F.P. Jiao, J.H. Jiang, X. Q. Chen, Removal, recovery and enrichment of metals from aqueous solutions using carbon nanotubes, J. Radioanal. Nucl. Chem. 299 (2014) 1155–1163.

[108] M.I. Kandah, J.L. Meunier, Removal of nickel ions from water by multi-walled carbon nanotubes, J. Hazard. Mater. 146 (2007) 283-288.

[109] Y.H. Li, F.Q. Liu, B. Xia, Q.J. Du, P. Zhang, D.C. Wang, Z.H. Wang, Y. Z. Xia, Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites, J. Hazard. Mater. 177(2010) 876-880.

[110] Y. Ge, Z. Li , D. Xiao, P. Xiong, N. Ye, Sulfonated multi-walled carbon nanotubes for the removal of copper (II) from aqueous solutions, J. Ind. Eng. Chem. 20 (2014) 1765–1771.

[111] X. Ren, J. Li , X. Tan, X. Wang, Comparative study of graphene oxide, activated carbon and carbon nanotubes as adsorbents for copper decontamination, Dalton Trans. 42 (2013) 5266–5274.

[112] B. Tawabini, S. A. Khaldi, M. Atieh, M. Khaled, Removal of mercury from water by multi-walled carbon nanotubes, Water Sci. Technol. 61(2010) 591-598.

[113] M. J. Shadbad, A. Mohebbi, A. Soltani, Mercury(II) removal from aqueous solutions by adsorption on multi-walled carbon nanotubes, Korean J. Chem. Eng. 28(2011) 1029-1034.

[114] B.S. Tawabini, S.F. A. Khaldi, M.M. Khaled, M.A. Atieh, Removal of arsenic from water by iron oxide nanoparticles impregnated on carbon nanotubes, J Environ Sci Health A Tox Hazard Subst Environ Eng. 46(2011) 215-223.

[115] S. A. Ntim, S. Mitra, Removal of trace arsenic to meet drinking water standards using iron oxide coated multiwall carbon nanotubes, *J. Chem. Eng. Data.* 56 (2011) 2077–2083.

[116] K. Shin, J. Hong, J. Jang, Heavy metal ion adsorption behavior in nitrogen-doped magnetic carbon nanoparticles: Isotherms and kinetic study, J. Hazard. Mater. 190(2011) 36-44.

[117] S. Vellaichamy, K. Palanivelu, Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture, J. Hazard. Mater. 185 (2011) 1131-1139.

[118] Q. Wang, J. Li, C. Chen, X. Ren, J. Hu, X. Wang, Removal of cobalt from aqueous solution by magnetic multiwalled carbon nanotube/iron oxide composites, Chem. Eng. J.174 (2011) 126– 133.

[119] H. Chen, J. Li, D. Shao, X. Ren, X. Wang, Poly(acrylic acid) grafted multiwall carbon nanotubes by plasma techniques for Co(II) removal from aqueous solution, Chem. Eng. J. 210 (2012) 475–481.

[120] V. K. Gupta, O. Moradi, I. Tyagi, S. Agarwal, H. Sadegh, R. S. Ghoshekandi, A. S. H. Makhlouf, M. Goodarzi, A. Garshasbi, Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review, Crit. Rev. Env. Sci. Technol. (2015) DOI: 10.1080/10643389.2015.1061874.

[121] H. Dai, Carbon nanotubes: opportunities and challenges, Surface Sci. 500 (2002) 218-241.

[122] Y.L. Zhao, J.F.R. Stoddart, Noncovalent functionalization of single-walled carbon nanotubes, Acc. Chem. Res. 42(2009) 1161-1171.

[123] K. Balasubramanian, M. Burghard, Chemicaly functionlazied carbon nanotubes, Small (2005)180-192.

[124] S. Iijima, Helical microtubules of graphitic carbon, Nature 354(1991) 56–58.

[125] X. Wang, Q. Li, J. Xie, Z. Jin, J. Wang, Y. Li, K. Jiang, S. Fan, Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates, Nano Lett. 9 (2009) 3137–3141.

[126] C.L. Chen, X.K. Wang, Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes, Ind. Eng. Chem. Res. 45(2006) 9144–9149.

[127] Ihsanullah, T. Laoui, A.M. Al-Amer, A. B. Khalil, A. Abbas, M. Khraisheh, M. A. Atieh. Novel anti-microbial membrane for desalination pretreatment: A silver nanoparticle-doped carbon nanotube membrane, Desalination 376 (2015) 82-93.

[128] Ihsanullah, A.M. Al-Amer, T. Laoui, A. Abbas, N. A. Aqeeli, F. Patel, M. Khraisheh, M. A. Atieh, N. Hilal, Fabrication and antifouling behaviour of a carbon nanotube membrane, Mater. Design 89 (2016) 549-558.

[129] X. Ren, C. Chena, M. Nagatsu, X. Wang, Carbon nanotubes as adsorbents in environmental pollution management: A review, Chem. Eng. J. 170 (2011) 395–410.

[130] S. M. Al-Hakami, A. B. Khalil, T. Laoui, M. A. Atieh, Fast disinfection of escherichia coli bacteria using carbon nanotubes interaction with microwave radiation, Bioinorg. Chem. Appl. (2013) 458943. doi:10.1155/2013/458943.

[131] C.H. Chen, C.C. Huang, Hydrogen adsorption in defective carbon nanotubes, Sep. Purif. Technol. 65(2009) 305–310.

[132] A. Gaur, M. Shim, Substrate-enhanced O_2 adsorption and complexity in the Raman G-band spectra of individual metallic carbon nanotubes, Phys. Rev. B 78(2008) 125422.

[133] K.M. Varlot, E. McRae, N.D. Pavlovsky, Comparative adsorption of simple molecules on carbon nanotubes dependence of the adsorption properties on the nanotube morphology, Appl. Surf. Sci. 196 (2002) 209–215.

[134] S. M.Gatica, M.J. Bojan, G. Stan, M.W. Cole, Quasi-one- and two-dimensional transitions of gases adsorbed on nanotube bundles, J. Chem. Phys. 114(2001) 3765–3769.

[135] J. Goering, E. Kadossov, U. Burghaus, Adsorption kinetics of alcohols on single-wall carbon nanotubes: an ultrahigh vacuum surface chemistry study, J. Phys. Chem. C 112 (2008)10114–10124.

[136] H. Hyung, J. H. Kim, Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters, Environ. Sci. Technol. 42(2008) 4416–4421.

[137] Ihsanullah, H. A. Asmaly, T. A. Saleh, T. Laoui, V. K. Gupta, M. A. Atieh, Enhanced adsorption of phenols from liquids by aluminum oxide/carbon nanotubes: Comprehensive study from synthesis to surface properties, J Mol. Liq. 206 (2015) 176-182.

[138] H. A. Asmaly, B. Abussaud, Ihsanullah, T. A. Saleh, V. K. Gupta, M. A. Atieh, Ferric oxide nanoparticles decorated carbon nanotubes and carbon nanofibers: from synthesis to enhanced removal of phenol, J. Saudi Chem. Soc. 19 (2015) 511-520.

[139] H. A Asmaly, B. Abussaud, Ihsanullah, T. A. Saleh, A. A. Bukhari, T. Laoui, A. M. Shemsi, V. K. Gupta, M. A. Atieh. Evaluation of micro and nano carbon-based adsorbents for the removal of phenol from aqueous solutions. Toxicol. Environ. Chem. 97 (2015) 1164-1179.

[140] C.L. Chen, J. Hu, D. Xu, X.L. Tan, Y.D. Meng, X. K. Wang, Surface complexation modeling of Sr(II) and Eu(III) adsorption onto oxidized multiwall carbon nanotubes, J. Colloid Interface Sci. 323(2008) 33–41.

[141] X. Wang, C. Chen, W. Hu, A. Ding, D. Xu, X. Zhou, Sorption of ^{243}Am(III) to Multiwall Carbon Nanotubes, Environ. Sci. Technol. 39 (2005) 2856-2860

[142] C. L. Chen, X. K. Wang, M. Nagatsu, Europium adsorption on multiwall carbon nanotube/iron oxide magnetic composite in the presence of polyacrylic acid, Environ. Sci. Technol. 43 (7) (2009) 2362–2367.

[143] D.D. Shao, Z.Q. Jiang, X.K. Wang, J.X. Li, Y.D. Meng, Plasma induced drafting carboxymethyl cellulose on multiwalled carbon nanotubes for the removal of UO_2^{2+} from aqueous solution, J. Phys. Chem. B 113 (2009) 860–864.

[144] S. Agnihotri, J.P.B Mota, R.M. Abadi, M.J. Rood, Structural characterization of single-walled carbon nanotube bundles by experiment and molecular simulation, Langmuir 21 (2005) 896–904.

[145] S. Talapatra, A.Z. Zambano, S.E. Weber, A.D. Migone, Gases do not adsorb on the interstitial channels of closed-ended single-walled carbon nanotube bundles, Phys. Rev. Lett. 85(2000)138–141.

[146] M. Muris, N. Dufau, M. Bienfait, N.D. Pavlovsky, Y. Grillet, J.P. Palmari, Methane and krypton adsorption on single-walled carbon nanotubes, Langmuir 16 (2000) 7019–7022.

[147] M. Muris, N.D. Pavlovsky, M. Bienfait, P. Zeppenfeld, Where are the molecules adsorbed on single-walled nanotubes? Surf. Sci. 492(2011) 67–74.

[148] A. Fujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, S. Suzuki, Y. Achiba, Gas adsorption in the inside and outside of single-walled carbon nanotubes, Chem. Phys. Lett. 336(2011) 205–211.

[149] O. Byl, P. Kondratyuk, S.T. Forth, S.A. FitzGerald, L. Chen, J.K. Johnson, J.T.Y. Jr, Adsorption of CF_4 on the internal and external surfaces of opened single-walled carbon nanotubes: a vibrational spectroscopy study, J. Am. Chem. Soc. 125(2003) 5889–5896.

[150] J.V. Pearce, M.A. Adams, O.E. Vilches, M.R. Johnson, H.R. Glyde, One-dimensional and two-dimensional quantum systems on carbon nanotube bundles, Phys. Rev. Lett. 95 (2005) 185302.

[151] M. Bienfait, P. Zeppenfeld, N.D. Pavlovsky, M. Muris, M.R. Johnson, T. Wilson, M. DePies, O.E. Vilches, Thermodynamics and structure of hydrogen, methane, argon, oxygen, and carbon dioxide adsorbed on single-wall carbon nanotube bundles, Phys. Rev. B 70(2004) 035410.

[152] L. Heroux, V. Krungleviciute, M.M. Calbi, A.D. Migone, CF_4 on carbon nanotubes: physisorption on grooves and external surfaces, J. Phys. Chem. B 110(2006) 12597–12602.

[153] J.W. Jiang, S.I. Sandler, M. Schenk, B. Smit, Adsorption and separation of linear and branched alkanes on carbon nanotube bundles from configurational-bias Monte Carlo simulation, Phys. Rev. B 72(2005) 045447.

[154] M.R. LaBrosse, W. Shi, J.K. Johnson, Adsorption of gases in carbon nanotubes: are defect interstitial sites important?, Langmuir 24(2008) 9430–9439.

[155] M.R. Babaa, N.D. Pavlovsky, E. McRae, K.M. Varlot, Physical adsorption of carbon tetrachloride on as-produced and on mechanically opened single walled carbon nanotubes, Carbon 42(2004)1549–1554.

[156] J.T. Burde, M.M. Calbi, Physisorption kinetics in carbon nanotube bundles, J. Phys. Chem. C 111(2007) 5057–5063.

[157] D.S. Rawat, M.M. Calbi, A.D. Migone, Equilibration time: kinetics of gas adsorption on closed- and open-ended single-walled carbon nanotubes, J. Phys. Chem. C 111 (2007) 12980–12986.

[158] S. Agnihotri, J.P.B. Mota, M.R. Abadi, M.J. Rood, Theoretical and experimental investigation of morphology and temperature effects on adsorption of organic vapors in single-walled carbon nanotubes, J. Phys. Chem. B 110 (2006) 7640–7647.

[159] H. Ulbricht, J. Kriebel, G. Moos, T. Hertel, Desorption kinetics and interaction of Xe with single-wall carbon nanotube bundles, Chem. Phys. Lett. 363(2002) 252–260.

[160] M.R. Babaa, I. Stepanek, K.M. Varlot, N.D. Pavlovsky, E. McRae, P. Bernier, Opening of single-walled carbon nanotubes: evidence given by krypton and xenon adsorption, Surf. Sci. 531(2003) 86–92.

[161] H.J. Wang, A.L. Zhou, F. Peng, H. Yu, L.F. Chen, Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb(II) in aqueous solution, Mater. Sci. Eng. A 466 (2007) 201–206.

[162] H. Wang, N. Yan, Y. Li, X.H. Zhou, J. Chen, B.X. Yu, M. Gong, Q.W. Chen, Fe nanoparticle-functionalized multi-walled carbon nanotubes: one-pot synthesis and their applications in magnetic removal of heavy metal ions, J. Mater. Chem. 22 (2012) 9230-9236.

[163] S.G. Wang, W.X. Gong, X.W. Liu, Y.W., Yao, B.Y. Gao, Q.Y. Yue, Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes, Sep. Purif. Technol. 58 (2007) 17–23.

[164] C. Zhang, J. Sui, J. Li, Y. Tang, W. Cai, Efficient removal of heavy metal ions by thiol-functionalized superparamagnetic carbon nanotubes, Chem. Eng. J. 210 (2012) 45–52.

[165] C. Li, Y. Zhang, Wang X, Zhao J, Chen W. Removal and recovery of lead (II) ions from contaminated licorice extracts using oxidized multi-walled carbon nanotubes. J Nanosci. Nanotechnol. 11(2011) 9731-9736.

[166] J.X. Li, S.Y. Chen, G.D. Sheng, J. Hu, X.L. Tan, X.K. Wang, Effect of surfactants on Pb(II) adsorption from aqueous solutions using oxidized multiwall carbon nanotubes, Chem. Eng. J. 166 (2011) 551-558.

[167] X.W. Zhao, Q. Jia, N.Z. Song, W.H. Zhou, Y.S. Li, Adsorption of Pb(II) from an aqueous solution by titanium dioxide/carbon nanotube nanocomposites: kinetics, thermodynamics, and isotherms, J. Chem. Eng. Data 55 (2010) 4428.

[168] X.M. Ren, D.D. Shao, G.X. Zhao, G.D. Sheng, J. Hu, S.T. Yang, X.K. Wang, plasma induced multiwalled carbon nanotube grafted with 2-vinylpyridine for preconcentration of pb(II) from aqueous solutions, Plasma Process Polym. 8 (2011) 589-598.

[169] L.Q. Ji, L.C. Zhou, X. Bai, Y.M. Shao, G.H. Zhao, Y.Z. Qu, C. Wang, Y.F. Li, Facile synthesis of multiwall carbon nanotubes/iron oxides for removal of tetrabromobisphenol A and Pb(II), J. Mater. Chem. 22(2012) 15853-15862.

[170] M. A. Tofighy, T. Mohammadi, Adsorption of divalent heavy metal ions from water using carbon nanotube sheets, J. Hazard. Mater. 185 (2011) 140–147.

[171] O. Moradi, The removal of ions by functionalized carbon nanotube: equilibrium, isotherms and thermodynamic studies, Chem. Biochem. Eng. Q. 25 (2011) 229–240.

[172] A. Stafiej, K. Pyrzynska, Adsorption of heavy metal ions with carbon nanotubes, Sep. Purif. Technol. 58 (2007) 49–52.

[173] M. A. Atieh, Removal of Chromium (VI) from polluted water using carbon nanotubes supported with activated carbon, Procedia Environ. Sci. 4 (2011) 281–293.

[174] Z. C. Di, J. Ding, X. J. Peng, Y. H. Li, Z. K. Luan, J. Liang, Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles, Chemosphere 62 (2006) 861–865.

[175] X.U.Y. Jun, R. Arrigo, L.I.U. Xi, S. D. Sheng, Characterization and use of functionalized carbon nanotubes for the adsorption of heavy metal anions, New Carbon Mater. 26 (2011) 57-62.

[176] A. S. K. Kumar, S.J. Jiang, W.L. Tseng, Effective adsorption of chromium(VI)/Cr(III) from aqueous solution using ionic liquid functionalized multiwalled carbon nanotubes as a super sorbent, J. Mater. Chem. A. 3(2015) 7044-7057.

[177] F. A. A. Khaldi, B. A. Sharkh, A. M. Abulkibash, M. A. Atieh, Cadmium removal by activated carbon, carbon nanotubes, carbon nanofibers, and carbon fly ash: a comparative study, Desalin. Water Treat. 53 (2015) 1417–1429.

[178] P. Liang,Y. Liu, L. Guo, J. Zeng, H. Lu, Multiwalled carbon nanotubes as solid-phase extraction adsorbent for the preconcentration of trace metal ions and their determination by inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom. 19 (2004) 1489–1492.

[179] H.H. Cho, K. Wepasnick, B. A. Smith, F. K. Bangash, D.H. Fairbrother, W. P. Ball, sorption of aqueous Zn[II] and Cd[II] by multiwall carbon nanotubes: the relative roles of oxygen-containing functional groups and graphenic carbon, Langmuir 26(2010) 967–981.

[180] Z. Velickovic, G.D. Vukovic, A.D. Marinkovic, M.S. Moldovan, A.A. P. Grujic, P.S. Uskokovic, M.D. Ristic, Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multiwall carbon nanotubes, Chem. Eng. J. 181 (2012) 174-181.

[181] P. H. Chen, C.F. Hsu, D. D.W. Tsai, Y.M. Lu, W.J. Huang, Adsorption of mercury from water by modified multiwalled carbon nanotubes: adsorption behaviour and interference resistance by coexisting anions, Environ. Technol. 35(2014) 1935–1944.

[182] A.H. E. Sheikh, Y.S.A. Degs, R.M.A. Asad, J.A. Sweileh, Effect of oxidation and geometrical dimensions of carbon nanotubes on Hg(II) sorption and preconcentration from real waters, Desalination 270 (2011) 214-220.

[183] J. Liang, J. Liu, X. Yuan, H. Dong, G. Zeng, H. Wu, H. Wang, J. Liu, S. Hua, S. Zhang, Z. Yu, X. He, Y. He, Facile synthesis of alumina-decorated multi-walled carbon nanotubes for simultaneous adsorption of cadmium ion and trichloroethylene, Chem. Eng. J. 273 (2015) 101–110.

[184] Z. Liu, L. Chen, Z. Zhang, Y. Li, Y. Dong, Y. Sun, Synthesis of multi-walled carbon nanotube–hydroxyapatite composites and its application in the sorption of Co(II) from aqueous solutions, J. Mol. Liq. 179 (2013) 46–53.

[185] H.A. Shawky, A.H.M.E. Aassar, D.E.A. Zeid, Chitosan/carbon nanotube composite beads: Preparation, characterization, and cost evaluation for mercury removal from wastewater of some industrial cities in Egypt, J. Appl. Polym. Sci. 125(2012) E93-E101.

[186] K. Pillay, E.M. Cukrowska, N.J. Coville, Improved uptake of mercury by sulphur-containing carbon nanotubes, Microchem. J. 108 (2013) 124-130.

[187] M. Hadavifar, N. Bahramifar, H. Younesi, Q. Li, Adsorption of mercury ions from synthetic and real wastewater aqueous solution by functionalized multi-walled carbon nanotube with both amino and thiolated groups, Chem. Eng. J. 237 (2014) 217–228.

[188] N. M. Bandaru, N. Reta, H. Dalal, A. V. Ellis, J. Shapter, N. H. Voelcker, Enhanced adsorption of mercury ions on thiol derivatized single wall carbon nanotubes, J. Hazard. Mater. 261 (2013) 534– 541.

[189] H. K. Moghaddam, M. Pakizeh, Experimental study on mercury ions removal from aqueous solution by MnO_2/CNTs nanocomposite adsorbent, J. Indus. Eng. Chem. 21 (2015) 221–229.

[190] A. Gupta, S.R. Vidyarthi, N. Sankararamakrishnan, Enhanced sorption of mercury from compact fluorescent bulbs and contaminated water streams using functionalized multiwalled carbon nanotubes, J. Hazard. Mater. 274 (2014) 132–144.

[191] C.H. Wu, Studies of the equilibrium and thermodynamics of the adsorption of Cu^{2+} onto as-produced and modified carbon nanotubes, J. Colloid. Interface Sci. 311 (2007) 338–346.

[192] G. Sheng, J. Li , D. Shao, J. Hu, C. Chen, Y. Chen, X. Wang, Adsorption of copper(II) on multiwalled carbon nanotubes in the absence and presence of humic or fulvic acids, J Hazard. Mater. 178 (2010) 333–340.

[193] W.W. Tang, G.M. Zeng, J.L. Gong, Y. Liu, X.Y. Wang, Y.Y. Liu, Z.F. Liu, L. Chen, X.R. Zhang, D.Z. Tu, Simultaneous adsorption of atrazine and Cu (II) from wastewater by magnetic multi-walled carbon nanotube, Chem. Eng. J. 211 (2012) 470-478.

[194] E. Salehi, S.S. Madaeni, L. Rajabi, V. Vatanpour, A.A. Derakhshan, S. Zinadini, S. Ghorabi, H. A. Monfared, Novel chitosan/poly(vinyl) alcohol thin adsorptive membranes modified with amino functionalized multi-walled carbon nanotubes for Cu(II) removal from water: Preparation, characterization, adsorption kinetics and thermodynamics, Sep. Purif. Technol. 89 (2012) 309–319.

[195] Y.H. Li, Z. Luan, X. Xiao, X. Zhou, C. Xu, D. Wu, B. Wei, Removal of Cu^{2+} ions from aqueous solutions by carbon nanotubes, Adsorpt. Sci. Technol. 21(2003) 475-485.

[196] C. Lu, H. Chiu, Adsorption of zinc (II) from water with purified carbon nanotubes, Chem. Eng. Sci. 61 (2006) 1138–1145.

[197] C. Lu, H. Chiu, C. Liu, Removal of zinc(II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies, Ind. Eng. Chem. Res. 45(2006) 2850-2855.

[198] M. A. Salam, M.S.I. Makki, M. Y.A. Abdelaal, Preparation and characterization of multi-walled carbon nanotubes/chitosan nanocomposite and its application for the removal of heavy metals from aqueous solution, J. Alloy. Compd. 509 (2011) 2582–2587.

[199] N.M. Mubarak, R.F. Alicia, E.C. Abdullah, J.N. Sahu, A.B. Ayu Haslija, J. Tan, Statistical optimization and kinetic studies on removal of Zn^{2+} using functionalized carbon nanotubes and magnetic biochar, J. Environ. Chem. Eng. 1 (2013) 486–495.

[200] C.Y. Lu, C.T. Liu, F.S. Su, Sorption kinetics, thermodynamics and competition of Ni^{2+} from aqueous solutions onto surface oxidized carbon nanotubes, Desalination 249 (2009) 18–23.

[201] C. Lu, C. Liu, G. P. Rao, Comparisons of sorbent cost for the removal of Ni^{2+} from aqueous solution by carbon nanotubes and granular activated carbon, J Hazard. Mater. 151(2008) 239–246.

[202] D.D. Shao, G.D. Sheng, C.L. Chen, X.K. Wang, M. Nagatsu, Removal of polychlorinated biphenyls from aqueous solutions using beta-cyclodextrin grafted multiwalled carbon nanotubes, Chemosphere 79 (2010) 679–685.

[203] D.D. Shao, Z.Q. Jiang, X.K. Wang, SDBS modified XC-72 carbon for the removal of Pb(II) from aqueous solutions, Plasma Process. Polym. 7 (2010) 552–560.

[204] C.Chen, B. Liang,A. Ogino, X. Wang, M. Nagatsu, Oxygen functionalization of multiwall carbon nanotubes by microwave-excited surface-wave plasma treatment, J. Phys. Chem. C 113 (2009) 7659–7665.

[205] C.Y. Lu, C.T. Liu, Removal of nickel(II) from aqueous solution by carbon nanotubes, J. Chem. Technol. Biotechnol. 81 (2006) 1932–1940.

[206] K. Pillay, E.M. Cukrowska, N.J. Coville, Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution, J. Hazard. Mater. 166 (2009) 1067–1075.

[207] J.P. Ruparelia, S.P. Duttagupta, A.K. Chatterjee, S. Mukherji, Potential of carbon nanomaterials for removal of heavy metals from water, Desalination 232 (2008) 145–156.

[208] Z.M. Gao, T.J. Bandosz, Z.B. Zhao,M. Han, J.S. Qiu, Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes, J. Hazard. Mater. 167 (2009) 357–365.

[209] D. Xu, X.L. Tan, C.L. Chen, X.K. Wang, Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes, J. Hazard. Mater. 154 (2008) 407–416.

[210] C. Lu, H. Chiu, H. Bai, Comparisons of adsorbent cost for the removal zinc(II) from aqueous solution by carbon nanotubes and activated carbon, J. Nanosci. Nanotechnol. 7 (2007) 1647–1652.

[211] L. Chiu-wing, J.T. James, R. McCluskey, S. Arepalli, R.L. Hunter, A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risks, Crit. Rev. Toxicol. 36 (2006) 189-217.

[212] V. K.K. Upadhyayula, S. Deng, M. C. Mitchell, G. B. Smith, Application of carbon nanotube technology for removal of contaminants in drinking water: A review, Sci. Total Environ. 408 (2009) 1–13.

[213] P. Wick, P. Manser, L.K. Limbach, U.D. Weglikowska, F. Krumeich, S. Roth, W.J.Stark, A. Bruinink, The degree and kind of agglomeration affect carbon nanotube cytotoxicity, Toxicol Lett. 168(2007)121–131.

[214] A. Magrez, S. Kasas, V. Salicio, N. Pasquier, J.W. Seo, M. Celio, S. Catsicas, B. Schwaller, L. Forró, Cellular toxicity of carbon-based materials, Nano Lett 6(200) 1121–1125.

[215] H. Dumortier, S. Lacotte, G. Pastorin , R. Marega , W. Wu, D. Bonifazi, J.P. Briand, M. Prato, S. Muller, A. Bianco, Functionalized carbon nanotubes are non-

cytotoxic and preserve the functionality of primary immune cells, Nano Lett. 6 (2006) 1522–1528.

[216] S. I. Al-Mayman, N. M. Al-Abbadi, M. A. Atieh, Thermal Oxidation Kinetic of Carbon Nanotubes (CNTs), Arab. J. Sci. Eng. 39 (2014) 621-630.

[217] A. A. Muataz, F. Ahmadun, C. Guan, E. Mahdi, A. Rinaldi, Effect of reaction temperature on the production of carbon nanotubes, Nano 1(2006) 251-257.

[218] C.L. Chen, B. Liang, D. Lu, A. Ogino, X.K. Wang, M. Nagatsu, Amino group introduction onto multiwall carbon nanotubes by NH_3/Ar plasma treatment, Carbon 48 (2010) 939–948.

[219] C.L. Chen, A. Ogino, X.K. Wang, M. Nagatsu, Plasma treatment of multiwall carbon nanotubes for dispersion improvement in water, Appl. Phys. Lett. 96 (2010) 131504.

[220] J. Hu, D.D. Shao, C.L. Chen, G.D. Sheng, J.X. Li, X.K. Wang, M. Nagatsu, Plasma induced grafting of cyclodextrin onto multiwall carbon nanotube/iron oxides for adsorbent application, J. Phys. Chem. B 114 (2010) 6779–6785.

[221] N. M. Mubarak, J. N. Sahu, E. C. Abdullah, N. S. Jayakumar, Removal of heavy metals from wastewater using carbon nanotubes, Sep. Purif. Rev. 43 (2014) 311–338.

[222] A. Khalid, A. A. Al-Juhani, O. C. Al-Hamouz, T. Laoui, Z. Khan, M. A. Atieh, Preparation and properties of nanocomposite polysulfone/multi-walled carbon nanotubes membranes for desalination, Desalination 367 (2015) 134–144.

CHAPTER 3

CARBON NANOTUBE MEMBRANES

Nanotechnology has shown great potential in water, wastewater treatment and desalination for providing environmentally acceptable water. Nanomaterials have many key physicochemical properties that make them suitable for water treatment and desalination. Various nanostructured materials like zeolites, metal/metal-oxide nanoparticles, dendrimers and carbon nanotubes (CNTs) have been widely employed in water purification. However, carbon nanotubes are considered as a versatile and unique material due to their extraordinary chemical and physical properties. CNTs have been rapidly explored among scientists in many fields e.g. chemistry, physics and material science owing to their unique properties such as low density, high aspect ratio, high chemical, thermal, and mechanical strength and remarkable electrical and optical properties.

CNTs have been widely employed for the removal of a number of contaminants from aqueous solutions [1-12]. Various experimental studies have reported the adsorption of heavy metal ions [1-6], small molecules like hydrogen and oxygen [7-9] and organic chemicals [10-12] on different CNTs.

3.1 Carbon Nanotube Membranes in Water Treatment

CNTs have recently attracted considerable attention for synthesis of novel membranes with attractive features for water purification [13]. CNTs can also be used as direct filters and effective fillers to improve the membrane performance. CNTs have proven to be

excellent filler in membrane due to improved permeability, rejection, disinfection and antifouling behavior. The flux through CNTs has been estimated to be 3-4 orders of magnitude faster than predicted by the Hagen-Poiseuille equation [13].

Typical inorganic membranes have been made of ceramic, carbon, silica, zeolite, various oxides and metals. These membranes have been employed in various applications including gas separations, separation of H_2O from chemical reaction mixtures and removal of dissolved salts and other contaminants from water. However, these membranes separate the components based on their sizes [14]. The carbon based membrane with CNT-iron oxide has the advantage to couple size based separation with the adsorption. The impregnated CNTs with metal oxide have excellent adsorptive properties for the removal of heavy metals and organic components [15-16].

In recent times, a number of studies have been carried out to investigate the molecular transport through CNTs and gaps between the CNTs bundles. The CNTs offers faster flow of molecules through it as compared to the other materials of same size [13]. The transport of liquid and gas molecules through CNTs is predicted by molecular dynamics simulation and also confirmed experimentally [17-18]. A typical schematic view of this phenomenon is shown in Fig. 3-1.

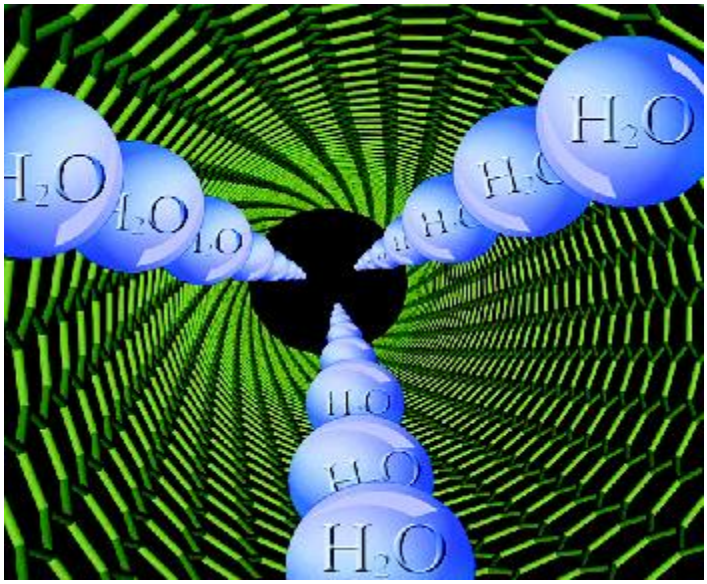

Figure 3-1: Water molecules passing quickly through the inner core of a carbon nanotube [13] (Reprint permission from Springer)

3.2 Types of CNT Membranes

In the literature, different approaches have been reported by researchers for the synthesis of CNT based membranes:

1. Template-prepared carbon nanotube membranes, in which carbonaceous materials are deposited inside pre-existing ordered porous membranes, e.g anodized alumina [13, 19-20].
2. Aligned-array outer-wall CNT membranes in which the interstices between vertical array of CNT serve as membrane [13, 21].
3. Composite membranes of aligned CNT/polymer or aligned CNT/ceramic [13, 22-23].
4. Buckypaper membranes [13, 24-26].
5. Multistacked membranes composed of bundles of vertically aligned CNTs [13].

6. Mixed-matrix membranes, where CNTs are used as fillers in a polymer matrix [27-32].

Among these categories, the mixed as mixed-matrix membrane has gained considerable attention due to ease of synthesis and broad applications. Different nanoparticles such as TiO_2 [33–37], Al_2O_3 [38–40], ZrO_2 [41], SiO_2 [42] can be employed as a filler material for the synthesis of mixed-matrix membranes with improved performance.

Several studies have shown successful application of CNTs in polymer matrix [26-27]. Addition of CNTs has reported to substantially increase the water flux due to hydrophilic surface and large surface pores of the membranes [28]. Moreover, the tensile strength and fouling resistance of the membranes were reported to increase with addition of CNTs.

3.2.1 Template-Prepared Carbon Nanotube Membranes

This technique involves the deposition of carbonaceous materials in a porous template. The carbonaceous materials are usually deposited in template at high temperature during the synthesis of CNTs. This method leads to synthesis of CNT membrane with the desired dimensions and pores [13, 19-20]. These membranes have great potential for application in size-based separation and as catalytic membrane reactors. A schematic representation and SEM image of template-assisted CNT membranes are shown in Figure 3-2.

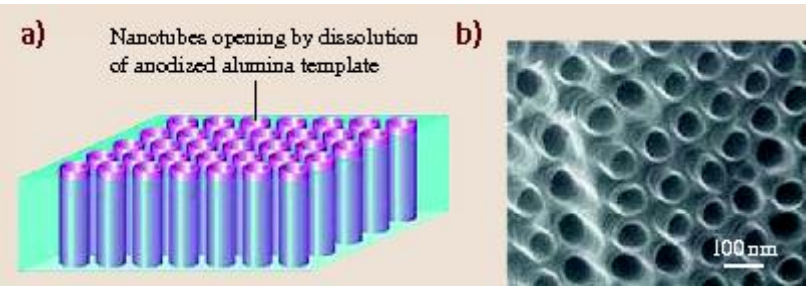

Figure 3-2: (a) CNTs grown inside anodized alumina template (b) SEM image of partial dissolution of the template [13] (Reprint permission from Springer)

3.2.2 Membranes with Aligned Arrays of CNTs

In the aligned arrays CNT membranes, CNTs are held together by van der Waals forces. The transport of molecules occurs mainly through the gaps/ interstices between the CNTs bundles. The typical pore size range of the membrane is 40–100 nm [13, 21]. Figure 3-3 shows schematic and SEM image of aligned arrays of CNTs [13].

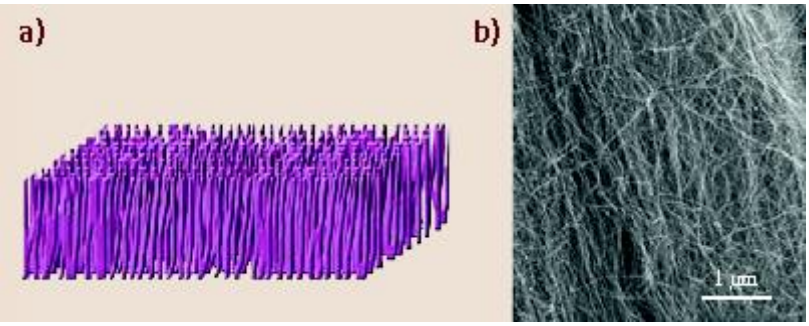

Figure 3-3: (a) Aligned CNTs membrane (b) SEM image of aligned arrays of dense nanotubes [13] (Reprint permission from Springer)

Studies have confirmed that electric potential can be used to render the hydrophobic nature of CNT to hydrophilic in these types of membranes. Electrical bias can be applied to control the water transport through membrane [13]. Srivastava et al. fabricated

macroscopic hollow cylinders having radically aligned CNTs walls as shown in Figure 3-4 [13, 21]. The cylinder length and diameter was in the range several centimeters. The hollow CNTs cylinders were synthesized by spray pyrolysis using ferrocene/benzene solution. The filter was able to separate efficiently some bacterial contaminants and different heavy hydrocarbons. The filter was easily cleaned via autoclaving and ultrasonication to regain the full efficiency [21].

A clear advantage of this filter is regaining of full efficiency after cleaning via ultrasonication and autoclaving. Furthermore, they can sustain higher temperature ≈400 °C than conventional polymer membrane, which can sustain temperature up to ≈52 °C only.

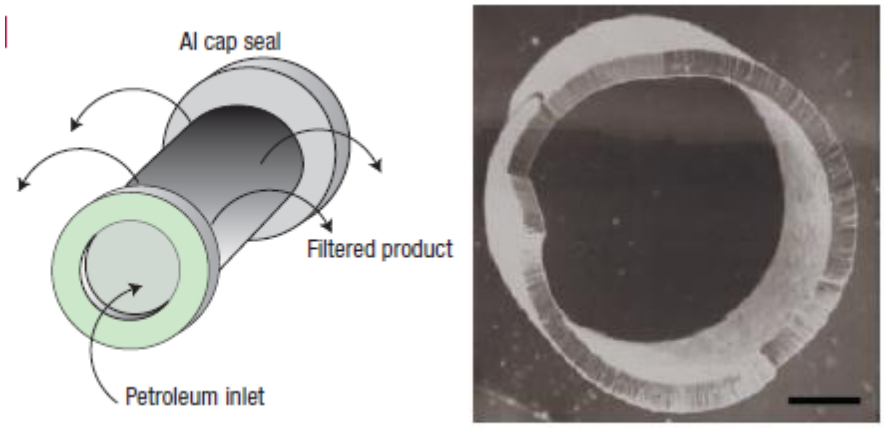

Figure 3-4: (a) Petroleum filtration set up using a membrane filter (b) SEM image of aligned tubes with radial symmetry [21] (Reprint permission from Nature Publishing Group)

3.2.3 Aligned CNT/Polymer Composite Membranes

In this approach, aligned array of open-ended CNTs are used to form a composite and space between the CNTs is filled with ceramic matrix [22], or inert polymer [23]. The

molecular transport occurs mainly through the open-ended CNTs. The selection of polymer is critical for this type of membrane. Polystyrene has been employed extensively due to its compatibility with the CNTs. Figure 3-5 shows a schematic and SEM image of open ended CNT membrane.

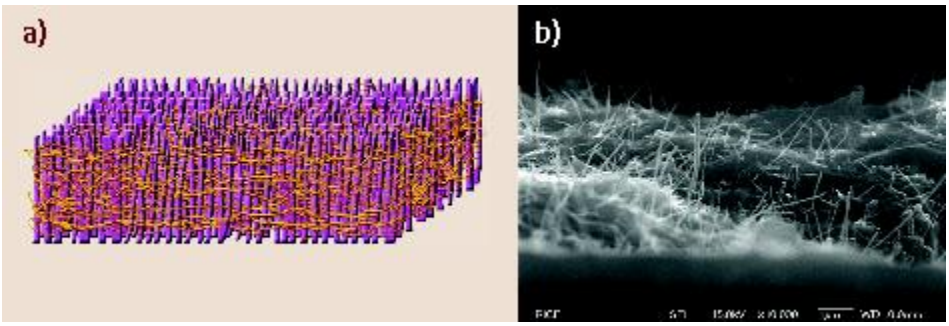

Figure 3-5: (a) Open ended CNT/Polymer composite membrane (b) SEM image of cross section of membrane with aligned CNTs [13, 30-31] (Reprint permission from Springer)

The ends of CNTs can be opened by plasma oxidation technique. This method results in the attachment of functional groups to the tips of CNTs as well as removal of various impurities from the surface. The typical pore size of membrane is in the range of 6-7 nm. Though open-ended CNT membranes fabrication is complex, but it offers tighter control over pore size [13].

3.2.4 Buckypaper Membrane

In this approach, membranes are synthesized by holding the CNTs via van der Waals interactions. In the first step, suspension of the CNTs in tetrahydrofuran (THF) is prepared, followed by the filtration under vacuum using polytetrafluoroethylene (PTFE) membrane. In second step, the sample is dried and thin sheet is removed from filter paper

[24-26]. Figure 3-6 shows schematic of the synthesis process and SEM image of buckypaper membrane.

The strength of buckypaper membrane is strongly dependent on the type of CNTs. Generally, higher tensile strength is achieved with pure and longer CNTs with less number of walls. As the number of walls of CNTs has increased, the mechanical strength is reduced due to less efficient van der Waals forces. A number of techniques have been reported in the literature for the improvement of mechanical strength of buckypaper membrane. The most common are graphitization [17], polymer intercalation [43], chemical treatment [44] and electron irradiation [45]. Buckypaper membranes have the advantage of high specific surface and are suitable for a number of water treatment applications.

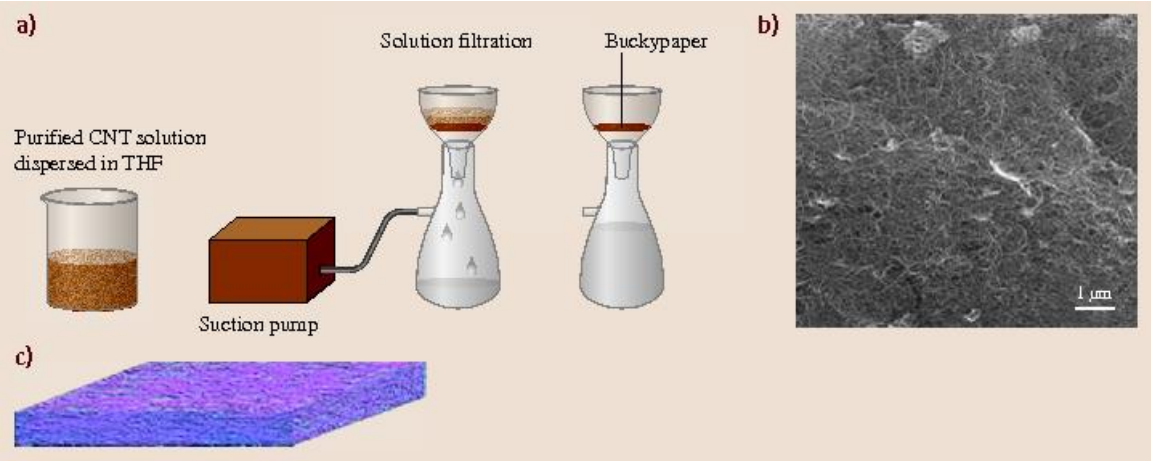

Figure 3-6: (a) Synthesis of buckypaper membrane (b) SEM image of buckypaper membrane with randomly oriented CNTs (c) Schematic of buckypaper membrane [13] (Reprint permission from Springer)

3.2.5 Multistacked Membranes of Aligned CNT bundles

In this process, a number of stacks of aligned CNT are grown during the synthesis of CNTs. Initially a single bundle of CNTs is grown from the carbon source using chemical vapor deposition technique. Using the same technique, the desired number of stacks is grown one above each other. This process offers the advantage of control over the length and density of CNTs. A thin layer of hydrophilic/hydrophobic material can also be used between the stack for desired applications. A schematic of the process and SEM are shown in Figure 3-7 [13].

The nanochannels can be used to filter a number of pollutants. Furthermore, the CNTs can be modified with carboxylic acids [46], amines, enzymes, and polyelectrolytes [47] to make it suitable for desired applications. Due to electrically conductive and chemically inert nature, these membranes also have potential applications as membrane reactors [48].

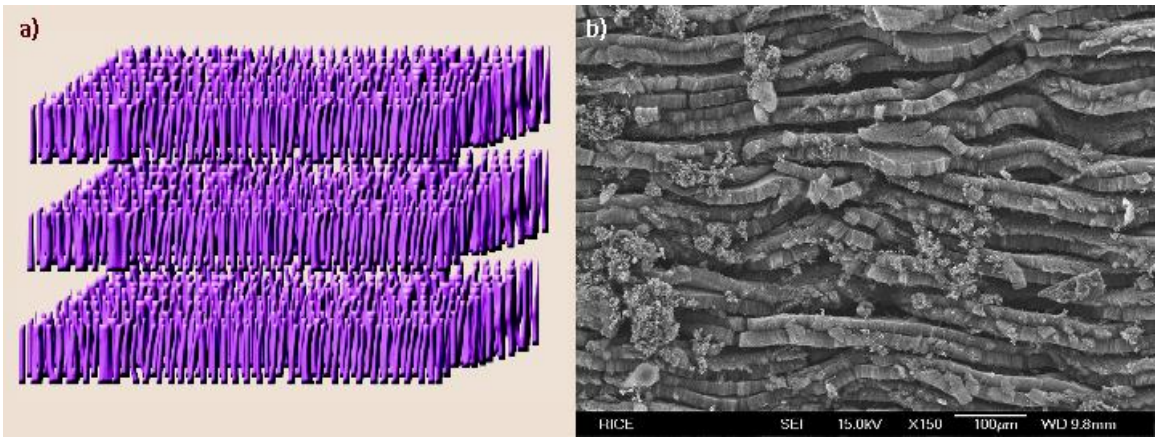

Figure 3-7: (a) Schematic representation, and (b) SEM image of the multistacked CNT membranes [13] (Reprint permission from Springer)

3.2.6 Mixed Matrix Membranes

Mixed matrix membranes have the advantage of low cost, mechanical strength and ease of fabrication. Generally, mixed matrix membranes couple the unique properties of inorganic materials and polymer matrix to yield new membrane with extraordinary properties. Inorganic materials are added to the traditional membranes to improve their properties such as selectivity, antifouling behavior and mechanical strength [41, 49-52].

Today, the use of nanoparticle as a fillers in mixed matrix membranes (also known as polymer–nanocomposite membranes) are emerging. These membranes utilize the properties of nanoparticles to improve the membrane characteristics. These nanoparticles have a number of applications in environment such as degradation of a number of pollutants from water [53-56].

Therefore, nanocomposite membranes are proved to have improved mechanical and thermal stability, high antifouling characteristics, enhanced flux and low cost compared to polymeric membranes [57-65]. In recent years, CNTs have been used as filler to synthesize the mixed matrix membranes [66-67].

CNTs offer a number of attractive features including antimicrobial and antifouling properties. However, CNTs tends to agglomerate due to van der Waals interaction, which limits their applications in some cases [68-69]. However, acid treated CNTs showed improved dispersion in the polymer matrix as compared to pristine CNTs [70]. Addition of CNTs was observed to improve the hydrophilicity of the membranes. This increase in hydrophilicity resulted in enhanced flux of water. CNTs addition has also shown a remarkable enhancement in the anti-fouling characteristics of the traditional polymer membranes [29].

Inorganic fillers are proven to enhance the mechanical and thermal stability of the traditional polymeric membranes. In pure polymeric membrane, compaction is a serious problem which declines the flux. This compaction occurs mainly due to macro-voids in the membranes [71]. The addition of fillers helped to improve the structure and hence mechanical strength of the membrane.

An alternative way to synthesize the mixed matrix membranes is to add polymers to the inorganic materials [72]. In these types of membranes, the polymer acts as filler while the inorganic materials work as a host matrix. Although still much research and advancement is needed to make these membranes commercially available, the initial results are encouraging. Table 3-1 highlighted the specific properties of some of the mixed matrix membranes.

Table 3-1: Properties of some of the common mixed matrix membranes

Membrane type	Particle amount (wt%)	Particle diameter/nm [length/µm]	Improved properties	Reference
Titania/PVDF	40	~27	1. Increased water flux 2. Low compaction 3. Improved thermal stability	[73]
Titania/SPES	8	~5	1. Minimize the formation of cake layer 2. Improved rejection 3. Low permeability	[74]
Titania/PES	~40 nm coating on surface	~5 to 24	1. Decreased rejection from ~78 to 65% 2. Increased flux nearly 50% 3. Increased hydrophilicity	[75]
Ag/PSf	4	~20 to 50	1. Reduced biofilm growth 2. Introduced antibacterial properties 3. Decreased rejection from ~82 to 70%	[57]

			4. Increased permeability 90%	
Zeolite/PSF		~250 to 300	1. Decreased flux decline 2. Improved mechanical stability 3. Low compaction	[76]
Silica/PSf	17	~34 to 130	1. Decreased flux decline 2. Decreased compaction under applied pressure 3. Increased mechanical stability	[76]
PANI/PSf	10	~43 [~0.259]	1. Increased flux 2-fold 2. Increased mechanical stability 3. Improved porosity and pore size 4. Improved hydrophilicity and surface roughness	[56]
Fe–Pd/PVDF	5	~20 to 30	1. Targeted dechlorination	[77]
CNT/PSf	0.5–4	~10 to 20 [~10 to 50]	1. The rejection and permeability depends strongly on the amount of the CNTs fillers 2. Increased hydrophilicity	[70]
CNT/PSf	4	~10 to 40 [~50]	1. Increased mechanical stability 2. Altered surface hydrophilicity 3. Increased surface roughness	[66]
Alumina/PVDF	19	~10	1. Increased flux over 40% 2. Increased mechanical stability 3. Increased hydrophilicity	[57]
Alumina/PES	0.01–0.05	~0.48	1. Flux decline was observed to decrease. 2. Increase in the amount of alumina leads to flux reduction 3. Rate of membrane fouling was observed to decrease	[58]

References

[1] C. Chen, J. Hu, D. Shao, J. Li, X. Wang, Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II), J Hazard Mater. 164 (2009) 923–928.

[2] Z. C.Di, Y.H. Li, Z.K. Laun, J. Liang, Adsorption of chromium(VI) ions from water by carbon nanotubes, Adsorpt Sci Technol. 22 (2004) 467–474.

[3] S.G. Wang, W.X. Gong, X.W. Liu, Y.W. Yao, B.Y. Gao, Q.Y. Yue, Removal of lead (II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes, Sep Purif Technol. 58 (2007) 17–23.

[4] Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes, Carbon 4 (2003) 2787–2792.

[5] C. Chen, X. Wang X, Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes, Ind Eng Chem Res. 45 (2006) 9144–9149.

[6] Ihsanullah**,** F. A. A. Khaldi, B. Abusharkh, M. Khaled, M.A. Atieh, M.S. Nasser, T. laoui, S. Agarwal, I. Tyagi, V. K. Gupta, Adsorptive removal of Cadmium (II) ions from liquid phase using acid modified carbon-based adsorbents, J Mol Liq. 204 (2015) 255-263.

[7] C.H. Chen, C.C. Huang, Hydrogen adsorption in defective carbon nanotubes, Sep Purif Technol. 65 (2009) 305–310.

[8] A. Gaur, M. Shim, Substrate-enhanced O_2 adsorption and complexity in the Raman G-band spectra of individual metallic carbon nanotubes, Phys Rev B. 78 (2008) 1254221-1254227.

[9] K.M. Varlot, E. McRae, N.D. Pavlovsky, Comparative adsorption of simple molecules on carbon nanotubes dependence of the adsorption properties on the nanotube morphology,Appl Surf Sci. 196 (2002) 209–215.

[10] J. Goering, E. Kadossov, U. Burghaus, Adsorption kinetics of alcohols on single-wall carbon nanotubes: an ultrahigh vacuum surface chemistry study, J Phys Chem C. 112 (2008) 10114–10124.

[11] H. Hyung, J.H. Kim, Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters, Environ Sci Technol. 42 (2008) 4416–4421.

[12] S. Iijima, T. Ichihashi, Y. Ando, Pentagons, heptagons and negative curvature in graphite microtubule growth, Nature 356 (1992) 776-778.

[13] A. Srivastava, S. Srivastava, K. Kalaga: Carbon Nanotube Membrane Filters, In Springer Handbook of Nanomaterials. Vajtai R, Ed. Berlin Heidelberg: Springer (2013) 1099–1116.

[14] R. Mallada, M. Menéndez, Inorganic Membranes: Synthesis, Characterization and Applications, 1st ed. Oxford: Elsevier (2008).

[15] V.K. Gupta, S. Agarwal, T. A. Saleh, Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal, J Hazard Mater. 185 (2011) 17–23.

[16] V. K. Gupta, S. Agarwal, T.A. Saleh, Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. Water Res. 45(6) (2011) 2207-2212.

[17] A.I. Skoulidas, D.M. Ackerman, J.K. Johnson, D.S. Sholl, Rapid transport of gases in Carbon nanotubes, Phys. Rev. Lett. 89 (2002) 185901.

[18] G. Hummer, J.C. Rasaiah, J.P. Noworyta, Water conduction through the hydrophobic channel of a carbon nanotube, Nature 414 (2001)188–190.

[19] S.A. Miller, V.Y. Young, C.R. Martin, Electroosmotic flow in template-prepared carbon nanotube membranes, J. Am. Chem. Soc. 123 (2001) 12335–12342.

[20] C. Wang, M. Li, S. Pan, H. Li, Well-aligned carbon nanotube array membrane synthesized in porous alumina template by chemical vapor deposition, Chin. Sci. Bull. 45 (2000) 1373–1376.

[21] A. Srivastava, O.N. Srivastava, S. Talapatra, R. Vajtai, P.M. Ajayan, Carbon nanotube filters, Nat. Mater. 3 (2004) 610–614.

[22] B.J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas, L.G. Bachas, Aligned multiwalled carbon nanotube membranes, Science 303 (2004) 62–65.

[23] J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P.Grigoropoulos, A. Noy, O. Bakajin, Fast mass transport through sub-2-nanometer carbon nanotubes, Science 312 (2006) 1034–1037.

[24] G.T. Pham, Y.B. Park, S. Wang, Z. Liang, B. Wang, C. Zhang, P. Funchess, L. Kramer, Mechanical and electrical properties of polycarbonate nanotube buckypaper composite sheets, Nanotechnology 19 (2008) 325705 (7pp).

[25] L.F. Dumée, K. Sears, J. Schütz, N. Finn, C. Huynh, S. Hawkins, M. Duke, S. Gray, Characterization and evaluation of carbon nanotube Bucky-Paper

membranes for direct contact membrane distillation, J. Membr. Sci. 351 (2010) 36–43.

[26] S.M. Cooper, H.F. Chuang, M. Cinke, B.A. Cruden, M. Meyyappan, Gas permeability of a buckypaper membrane, Nano Lett. 3 (2003) 189–192.

[27] Y. Ma, F. Shi, Z. Wang, M. Wu, J. Ma, C. Gao, Preparation and characterization of PSf/clay nanocomposite membranes with PEG 400 as a pore forming additive, Desalination 286 (2012) 131–137.

[28] K. Ebert, D. Fritsch, J. Koll, C. Tjahjawiguna, Influence of inorganic fillers on the compaction behaviour of porous polymer based membranes, J Membr Sci. 233 (2004) 71–78.

[29] S. Majeed, D. Fierro, K. Buhr, J. Wind, B. Du, A.B.D. Fierro, V. Abetz, Multi-walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes, J Membr Sci. 403-404 (2012) 101– 109.

[30] D.L. Arockiasamy, J. Alam, M. Alhoshan, Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications, Appl Water Sci. 3 (2013) 93–103.

[31] H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite, J Membr Sci. 362 (2010) 374–383.

[32] P. Shah, C.N. Murthy, Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal, J Membr Sci. 437 (2013) 90–98.

[33] J.B. Li, J.W. Zhu, M.S. Zheng, Morphologies and properties of poly(phthalazinone ether sulfone ketone) matrix ultrafiltration membranes with entrapped TiO_2 nanoparticles, J Appl Polym Sci. 103 (2006) 3623–3629.

[34] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li,The influence of nano-sized TiO_2 fillers on the morphologies and properties of PSf UF membrane, J Membr Sci. 288 (2007) 231–238.

[35] X. Cao, J. Ma, X. Shi, Z. Ren, Effect of TiO_2 nanoparticle size on the performance of PVDF membrane, Appl Surf Sci. 253 (2006) 2003–2010.

[36] S.J. Oh, N. Kim, Y.T. Lee, Preparation and characterization of PVDF/TiO_2 organic– inorganic composite membranes for fouling resistance improvement, J Membr Sci. 345 (2009) 13–20.

[37] R.A. Damodar, S.J. You, H.H. Chou, Study the self cleaning, antibacterial and photo catalytic properties of TiO_2 entrapped PVDF membranes, J Hazard Mater 72 (2009) 1321–1328.

[38] N.M. Wara, L.F. Francis, B.V. Velamakannim, Addition of alumina to cellulose acetate Membranes, J Membr Sci. 104 (1995) 43–49.

[39] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized Al_2O_3-particle addition on PVDF ultrafiltration membrane performance, J Membr Sci. 276 (2006) 162–167.

[40] F. Liu, M.R.M. Abed, K. Li, Preparation and characterization of poly(vinylidene fluoride)(PVDF) based ultrafiltration membranes using nano γ-Al_2O_3, J Membr Sci. 366 (2011) 97–103.

[41] A. Bottino, G. Capannelli, A. Comite, Preparation and characterization of novel porous PVDF-ZrO_2 composite membranes, Desalination 146 (2002) 35–40.

[42] S.P. Nunes, K.V. Peinemann, K. Ohlrogge, A. Alpers, M. Keller, A.T.N Pires, Membranes of poly(ether imide) and nano dispersed silica, J Membr Sci. 157 (1999) 219–226.

[43] J.N. Colemana, W.J. Blau, A.B. Dalton, E. Muñoz, S. Collins, B.G. Kim, J. Razal, M. Selvidge, G. Vieiro, R.H. Baughman, Improving the mechanical properties of single-walled carbon nanotube sheets by intercalation of polymeric adhesives, Appl. Phys. Lett. 82 (2003) 1682-1684.

[44] U. Dettlaff-Weglikowska, V. Skákalová, R. Graupner, S.H. Jhang, B.H. Kim, H.J. Lee, L. Ley, Y.W. Park, S. Berber, D. Tománek, S. Roth, Effect of $SOCl_2$ treatment on electrical and mechanical properties of single-wall carbon nanotube networks, J. Am. Chem. Soc. 127 (2005) 5125–5131.

[45] J.A. Åström, A.V. Krasheninnikov, K. Nordlund: Carbon nanotube mats and fibers with irradiation improved mechanical characteristics: A theoretical model, Phys. Rev. Lett. 93 (2004) 215503.

[46] H. Peng, L.B. Alemany, J.L.Margrave, V.N. Khabashesku: Sidewall carboxylic acid functionalization of single-walled carbon nanotubes, J. Am. Chem. Soc. 125 (2003)15174–15182

[47] A.M. Hollman, D. Bhattacharyya: Pore assembled multilayers of charged polypeptides in microporous membranes for ion Sep, Langmuir 20 (2004) 5418–5424.

[48] K.G. Denbigh, J.C.R. Turner: Chemical Reactor Theory: An Introduction, 3rd ed.

Cambridge Univ. Press, London (1984).

[49] P. Aerts, A. R. Greenberg, R. Leysen, W. B. Krantz, V. E. Reinsch and P. A. Jacobs, The influence of filler concentration on the compaction and filtration properties of Zirfon-composite ultrafiltration membranes, Sep. Purif. Technol. 22-23 (2001) 663–669.

[50] P. Aerts, S. Kuypers, I. Genne, R. Leysen, J. Mewis, I. F. J. Vankelecom and P. A. Jacobs, Polysulfone-ZrO_2 surface interactions. The influence on formation, morphology and properties of zirfon-membranes, J. Phys. Chem. B 110 (2006) 7425–7430.

[51] N. M. Wara, L. F. Francis and B. V. Velamakanni, Addition of alumina to cellulose-acetate membranes, J. Membr. Sci. 104 (1995) 43–49.

[52] I. Genne, S. Kuypers and R. Leysen, Effect of the addition of ZrO_2 to polysulfone based UF membranes, J. Membr. Sci. 113 (1996) 343–350.

[53] Y. C. Sharma, V. Srivastava, V. K. Singh, S. N. Kaul and C. H. Weng, Nano-adsorbents for the removal of metallic pollutants from water and wastewater, Environ. Technol. 30 (2009) 583–609.

[54] P. K. Stoimenov, R. L. Klinger, G. L. Marchin and K. J. Klabunde, Metal oxide nanoparticles as bactericidal agents, Langmuir, 18 (2002) 6679–6686.

[55] N. Savage and M. S. Diallo, Nanomaterials and water purification: opportunities and challenges, J. Nanopart. Res. 7 (2005) 331–342.

[56] Z. R. Yue, J. Economy, Nanoparticle and nanoporous carbon adsorbents for removal of trace organic contaminants from water, J. Nanopart. Res. 7 (2005) 477–487.

[57] L. Yan, Y. S. Li, C. B. Xiang, Preparation of poly(vinylidene fluoride)(PVDF) ultrafiltration membrane modified by nano-sized alumina (Al_2O_3) and its antifouling research, Polymer 46 (2005) 7701–7706.

[58] N. Maximous, G. Nakhla, W. Wan, K. Wong, Preparation, characterization and performance of Al_2O_3/PES membrane for wastewater filtration, J. Membr. Sci. 341 (2009) 67–75.

[59] Z. F. Fan, Z. Wang, M. R. Duan, J. X. Wang, S. C. Wang, Preparation and characterization of polyaniline/polysulfone nanocomposite ultrafiltration membrane, J. Membr. Sci. 310 (2008) 402–408.

[60] Z. F. Fan, Z. Wang, N. Sun, J. X. Wang, S. C. Wang, Performance improvement of polysulfone ultrafiltration membrane by blending with polyaniline nanofibers, J. Membr. Sci. 320 (2008) 363–371.

[61] J. R. Morones, J. L. Elechiguerra, A. Camacho, K. Holt, J. B. Kouri, J. T. Ramirez, M. J. Yacaman, The bactericidal effect of silver nanoparticles, Nanotechnology, 16 (2005) 2346–2353.

[62] T. H. Bae, T. M. Tak, Effect of TiO_2 nanoparticleson fouling mitigation of ultrafiltration membranes for activated sludge filtration, J. Membr. Sci. 249 (2005) 1–8.

[63] X. C. Cao, J. Ma, X. H. Shi, Z. J. Ren, Effect of TiO_2 nanoparticle size on the performance of PVDF membrane, Appl. Surf. Sci. 253 (2006) 2003–2010.

[64] J. F. Li, Z. L. Xu, H. Yang, L. Y. Yu, M. Liu, Effect of TiO_2 nanoparticles on the surface morphology and performance of microporous PES membrane, Appl. Surf. Sci. 255 (2009) 4725–4732.

[65] S. S. Hosseini, Y. Li, T. S. Chung, Y. Liu, Enhanced gas separation performance of nanocomposite membranes using MgO nanoparticles, J. Membr. Sci. 302 (2007) 207–217.

[66] L. Brunet, D. Y. Lyon, K. Zodrow, J. C. Rouch, B. Caussat, P. Serp, J. C. Remigy, M. R. Wiesner, P. J. J. Alvarez, Properties of membranes containing semi-dispersed carbon nanotubes, Environ. Eng. Sci. 25 (2008) 565–575.

[67] Y. Lin, M. Meziani,Y. Sun, Functionalized carbon nanotubes for polymeric nanocomposites, J. Mater. Chem. 17 (2007) 1143–1148.

[68] S. Kang, M. Pinault, L. D. Pfefferle and M. Elimelech, Single-walled carbon nanotubes exhibit strong antimicrobial activity, Langmuir, 23 (2007) 8670–8673.

[69] P. Ajayan, Nanotubes from carbon, Chem. Rev. 99 (1999) 1787–1800.

[70] J. H. Choi, J. Jegal, W. N. Kim, Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes, J. Membr. Sci. 284 (2006) 406–415.

[71] G. Jonsson, Methods for determining the selectivity of reverse osmosis membranes, Desalination, 24 (1978) 19–37.

[72] M. Kondo, M. Komori, H. Kita, K. Okamoto, Tubular-type pervaporation module with Zeolite NaA membrane, J. Membr. Sci. 133(1997) 133–141.

[73] K. Ebert, D. Fritsch, J. Koll, C. Tjahjawiguna, Influence of inorganic fillers on the compaction behaviour of porous polymer based membranes, J. Membr. Sci. 233 (2004) 71–78.

[74] T. H. Bae, I. C. Kim, T. M. Tak, Preparation and characterization of fouling-resistant TiO_2 self-assembled nanocomposite membranes, J. Membr. Sci. 275 (2006) 1–5.

[75] M. L.Luo, J. Q.Zhao,W.Tang, C. S.Pu,Hydrophilicmodification of poly(ether sulfone) ultrafiltration membrane surface by selfassembly of TiO_2 nanoparticles, Appl. Surf. Sci. 249 (2005) 76–84.

[76] M. M. Pendergast, J. M. Nygaard, A. K. Ghosh, E. M. V. Hoek, Using nanocomposite membrane materials to understand and control reverse osmosis membrane compaction, Desalination, 261 (2010) 255–263.

[77] V. Smuleac, L. Bachas, D. Bhattacharyya, Aqueous-phase synthesis of PAA in PVDF membrane pores for nanoparticle synthesis and dichlorobiphenyl degradation, J. Membr. Sci. 346 (2009) 310–317.

CHAPTER 4

FABRICATION AND ANTIFOULING BEHAVIOUR OF A CARBON NANOTUBE MEMBRANE

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Abstract

In this work, a novel approach is used to synthesize an iron oxide doped carbon nanotube (CNT) membrane, with the goal of fully utilizing the unique properties of CNTs. No binder is used for the synthesis of the membrane; instead, iron oxide particles serve as a binding agent for holding the CNTs together after sintering at high temperature. The produced membrane exhibited a high water flux and strong fouling resistance. In the first step, CNTs were impregnated with various loadings of iron oxide (1, 10, 20, 30 and 50%) via wet chemistry techniques. Impregnated CNTs were then compacted at 200 MPa and sintered at 1350 °C for 5 h to form a compact disc. The membranes were analysed by measuring their porosity, contact angle, diametrical compression test and water flux. The flux of pure water was observed to increase with an increase in iron oxide content. The permeate flux and rejection rate of sodium alginate (SA) were determined to predict the antifouling behavior of the membrane. A maximum removal of 90 and 88% of SA was achieved for membranes with a 10 and 1% iron oxide content, respectively, after 3 h. A minor decline in the permeate flux was observed for all membranes after 4 h of operation.

Keywords: *Membrane, iron oxide, water treatment, carbon nanotubes, sodium alginate*

4.1 Introduction

Water is the lifeblood of the modern era as a result of the scarcity of resources, drought and expansion of deserts. Reliable access to safe and clean drinking water is considered to be one of the most basic humanitarian goals and remains a major challenge in the 21st century. A report from the United Nations (UN) indicates that 1800 million people will face absolute water scarcity and two-thirds of the world population could be under stress conditions by 2025 [1, 2].

The reuse, recycling and recovery of water has proven to be successful and effective in creating a new and reliable water supply while not compromising public health. Membrane filtration is considered among the most promising and widely used processes for water treatment and desalination [1, 2].

Membranes are classified into different types based on their nominal size or molecular weight cut-off (MWCO), including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Microfiltration is employed for suspended solids, protozoa, and bacteria removal; ultrafiltration for virus and colloid removal; nanofiltration for heavy metals dissolved in organic matter and hardness removal; and reverse osmosis for desalination, water reuse, and ultrapure water production [3].

Membranes can also be classified based on their configurations, including hollow fibre, spiral, plate and frame, and tubular. Membranes are manufactured from ceramic, polymeric, or hybrid materials. The most common polymeric membranes are poly(sulfone), poly(amide), poly(propylene), poly(tetrafluoroethylene), cellulose acetate, and poly(vinylidene) fluoride. Most of the ceramic membranes are made using metal oxides including aluminium oxide (Al_2O_3) and titanium oxide (TiO_2), as well as silica

(SiO_2), zeolites, microporous carbon, silicon carbide (SiC) and zirconia (ZrO_2). Ceramic membranes are well suited for challenging water purification processes due to their chemical and thermal stabilities. However, ceramic membranes are typically considered too expensive and are recommended only for small scale operations. Polymeric membranes, on the other hand, dominate the current water desalination and purification market because of their excellent mechanical strength under pressure and their high selectivity. However, in many wastewater applications, the current polymeric membranes are less fouling-resistant and chemically stable than ceramic membranes [4].

Typical inorganic membranes are made of ceramic, carbon, silica, zeolite, various oxides and metals. These membranes have been employed in various applications, including gas separation, separation of H_2O from chemical reaction mixtures and the removal of dissolved salts and other contaminants from water. However, these membranes separate the components based on their size [5].

Carbon nanotubes (CNTs) have been rapidly explored among scientists in many fields, including chemistry, physics and material science, owing to their unique properties, such as high aspect ratio, low density, high chemical, thermal, and mechanical strength, and remarkable electrical and optical properties. CNTs have been widely employed for the removal of various contaminants from aqueous solutions. Various experimental studies have reported the adsorption of heavy metal ions [6-13], small molecules like hydrogen and oxygen [14-15] and organic chemicals [16-19] on different CNTs.

CNTs have recently attracted considerable attention for the synthesis of novel membranes with attractive features for water purification [20-36]. CNTs can also be used as direct

filters and effective fillers to improve the membrane performance. CNTs have proven to be excellent fillers in membranes due to improved permeability, rejection, disinfection and antifouling behaviour. The flux through CNTs has been estimated to be 3-4 orders of magnitude faster than predicted by the Hagen-Poiseuille equation [22-24].

In recent times, the mixed-matrix membrane has been explored extensively due to its ease of synthesis and broad applications. Various nanoparticles, such as TiO_2 [37-38], Al_2O_3 [39–40], ZrO_2 [41], and SiO_2 [42], can be employed as filler materials for the synthesis of mixed-matrix membranes with improved performance. CNTs are also appealing membrane fillers and act as extraordinary mass transport channels as studied by various research groups. Several studies have shown successful application of CNTs in a polymer matrix [33-35, 43-46]. The addition of CNTs has been reported to substantially increase the water flux due to the hydrophilic surface and large surface pores of the membranes [35]. Moreover, the tensile strength and fouling resistance of the membranes were reported to increase with the addition of CNTs.

The presence of natural organic matter, microorganisms and high concentration of salt in water systems leads to membrane fouling. Typical adverse effects of membrane fouling include (i) a reduction in the membrane water flux, (ii) an increase in the solute concentration polarization, (iii) increased energy requirements; (iv) biodegradation and/or biodeterioration of the membrane materials, (v) an increase in the module differential pressure, and (vi) the establishment of concentrated populations of primary or secondary human pathogens on the membrane [5]. Therefore, fouling is a major obstacle in the widespread application of membrane technology. Several studies have been performed in

recent years with the goal of enhancing the fouling resistance of membranes by surface modification with CNTs [5, 47].

This paper describes a novel synthesis concept of a carbon nanotube metal oxide membrane, comprising dispersed CNTs and iron oxide nanoparticles. In the first step, CNTs are impregnated with different amounts of iron oxide (1, 10, 20, 30 and 50%) via a wet chemistry technique. The impregnated CNTs are then compacted and sintered to form a compact disc. The effect of the iron oxide content, compaction force and sintering temperature on the membrane properties was studied. The powder materials were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and thermogravimetric analysis (TGA), while the prepared membranes were analysed by measuring their density, pore size, contact angle measurement and water flux. CNT-iron oxide membranes are expected to efficiently remove heavy metals from water in a continuous flow system. The permeate flux and rejection rate of sodium alginate (SA) were determined to predict the antifouling behaviour of the membrane.

4.2 Experimental Details

4.2.1 Materials

The carbon nanotubes used in this study were supplied by Chengdu Organic Chemicals Co. Ltd. (China). The CNT specifications are shown in Table 4-1. Iron (III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$ (Reagent grade, Sigma Aldrich, purity ≥ 98%) was used as a metal oxide salt for iron oxide.

The iron oxide nanoparticles were impregnated on the surface of CNTs by a wet impregnation method. For example, for a 1% iron oxide loading, 1.443 g of pure ferric nitrate [$Fe(NO_3)_3.9H_2O$] was dissolved in 500 mL of ethanol (98% purity). CNTs (19.88 g) were also dissolved in the 400 mL of absolute ethanol. Both solutions were sonicated for 45 min separately before being mixed together. The resultant mixture was again sonicated for 1 h at room temperature. The aim of ultrasonication is to have complete and homogeneous wetting of the particles during impregnation; this decreases the likelihood of agglomeration, which occurs due to the formation of clumps of liquid. The mixture was then kept in an oven to evaporate the ethanol. The residue was then calcinated for 3.5 h at 350 °C in a furnace to obtain CNTs impregnated with 1% iron oxide. This process leads to homogenously dispersed iron oxide nanoparticles in a CNT matrix, and the attachment of iron oxide to the CNTs. Similarly, CNTs were doped with different iron oxide loadings, i.e., 10, 20, 30 and 50 %.

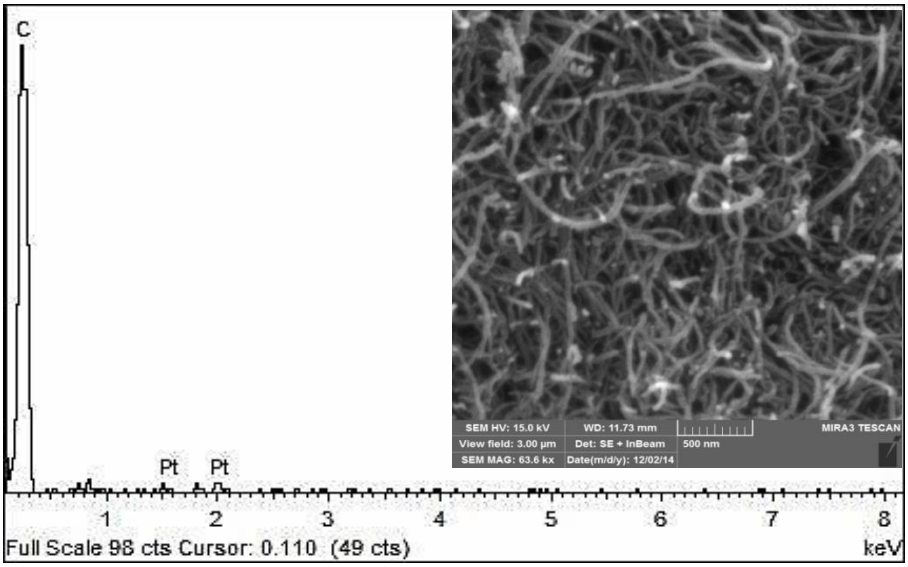
Table 4-1: Chemical and physical properties of the carbon nanotubes

Property	**Value**
Outer diameter (nm)	10-30
Length (μm)	1-10
Purity	>95%
Ash	<1.5 weight%
Specific surface area (m^2/g)	> 200
Electrical conductivity (S/cm)	$>10^2$

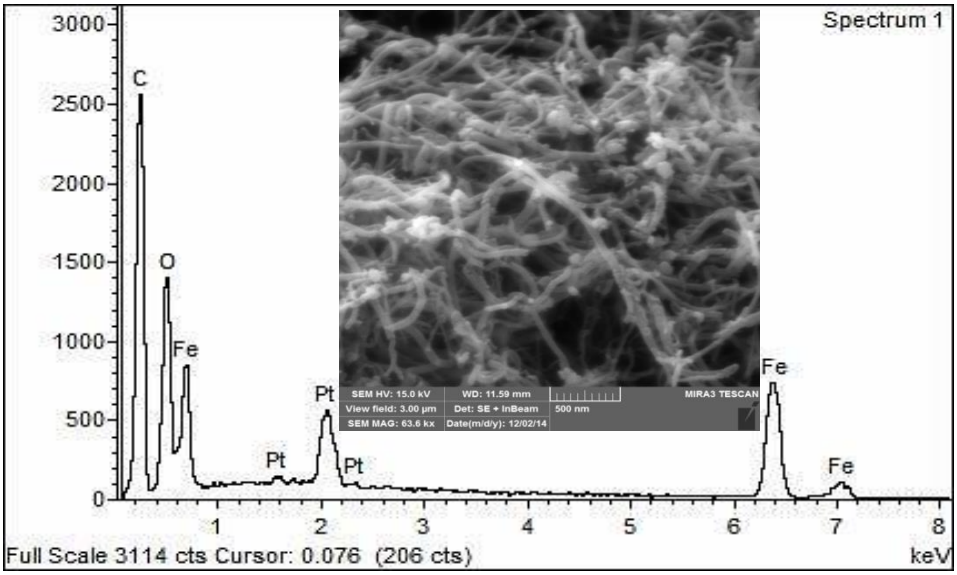
4.3 Characterization

4.3.1 SEM, TEM and EDS Analysis of Raw and Impregnated CNTs

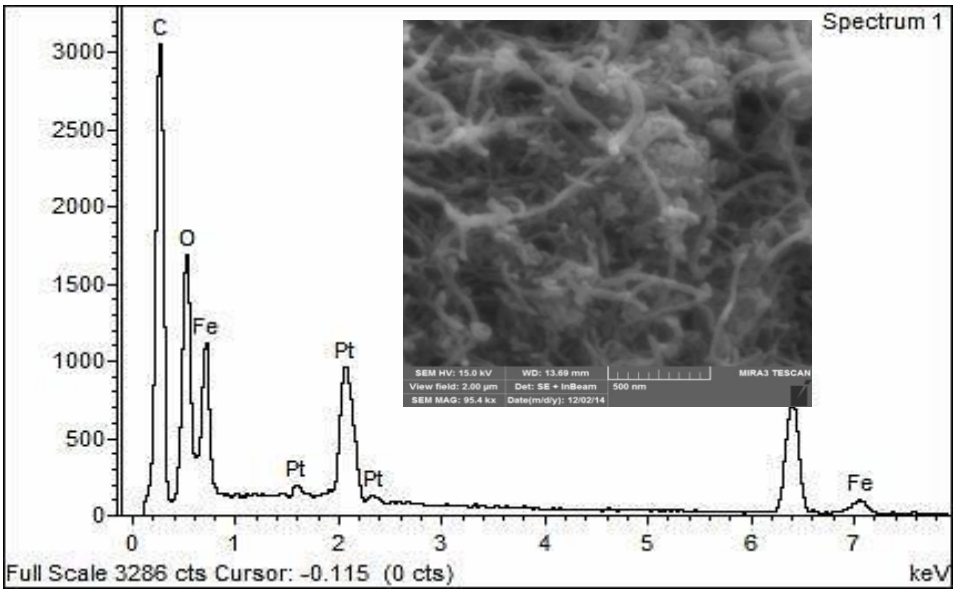
Fig. 4-1 displays the SEM images and EDS spectra of the CNTs and CNT-Fe_2O_3. The presence of the iron oxide particles was confirmed by EDS analysis. High-resolution transmission electron microscopy (HRTEM) was performed to characterize the structure and size of the nanotubes and iron oxide nanoparticles and to observe the configuration adopted by the iron oxide nanoparticles on the surfaces of the CNTs (as shown in Fig. 4-2). The HRTEM image of the unmodified nanotubes is presented in Fig. 4-2a. This image shows hollow and tubular nanotubes with an outer diameter of 10-30 nm and an inner diameter of 5-10 nm. Figure 4-2b shows a typical HRTEM image of CNT-Fe_2O_3 indicating the presence of the iron oxide nanoparticles with an average size of ~3 nm on the surfaces of the CNTs. It was also noted that the structure of the CNTs was not damaged during the nanoparticle impregnation process.



(a) Raw CNTs



(b) 20 % CNT-Fe_2O_3



(c) 50 % CNT-Fe_2O_3

Figure 4-1: SEM and EDS analysis of (a) Raw CNTs, (b) 20% CNT-Fe_2O_3 and (c) 50% CNT-Fe_2O_3

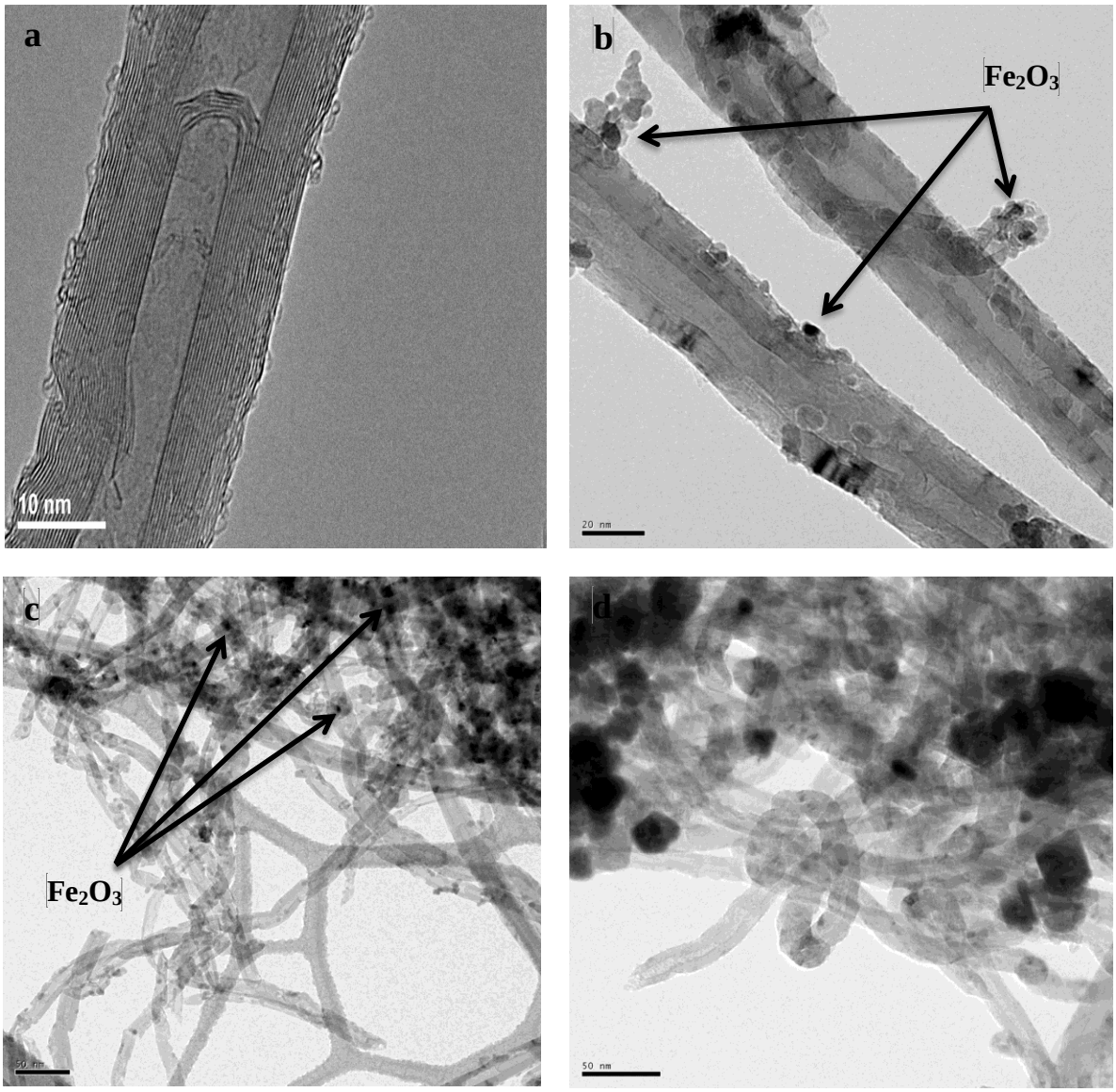


Figure 4-2: HRTEM images of (a) Raw CNTs and (b, c and d) CNT-Fe_2O_3

4.3.2 Thermal Degradation Analysis

Thermogravimetric analysis (TGA) is an effective technique to evaluate the quality of the CNTs. The metal impurity content associated with the CNTs can be determined by simply burning the CNT samples in air. Fig. 4-3 displays the TGA curves for the CNTs and CNT-Fe_2O_3 under air at a heating rate of 10 °C/min. It was observed that the raw CNTs did not undergo any major mass loss before ~500°C; however, a sharp weight loss was observed thereafter. This weight loss is attributed to the degradation of disordered or amorphous carbon, moisture, ash, and other metal impurities [48-51]. It has also been reported by many researches that amorphous carbon has a low thermal stability due to its lower activation energy for oxidation. The degradation of CNTs at temperatures higher than 500°C corresponds to the thermal oxidation of the remaining disordered carbon [50-51].

For the impregnated CNTs (CNT-Fe_2O_3), the initial oxidation and final oxidation temperatures were observed to decrease. The presence of iron oxide nanoparticles reduced the initial and final degradation temperature of the CNTs by almost 100 °C as shown in Fig.3. The lower thermal stability of the impregnated CNTs when compared to the raw CNTs may be due to the attachment of iron oxide particles to the walls of the CNTs. The lower degradation temperature of iron oxide compared to the raw CNTs leads to the faster degradation of the impregnated CNTs.

TGA was also used to estimate the quantitative loading of Fe_2O_3 onto the CNT surface by weighing the residual matter, which consists of Fe_2O_3 predominantly after the CNTs have been burnt off completely in air. No residual weight was measured after the complete oxidation of raw CNTs; while the weight of CNT samples with 1, 10, 20, 30 and 50%

Fe_2O_3 were reduced to 1.2, 11, 22, 32 and 53%, respectively, after being heated at 900°C in air.

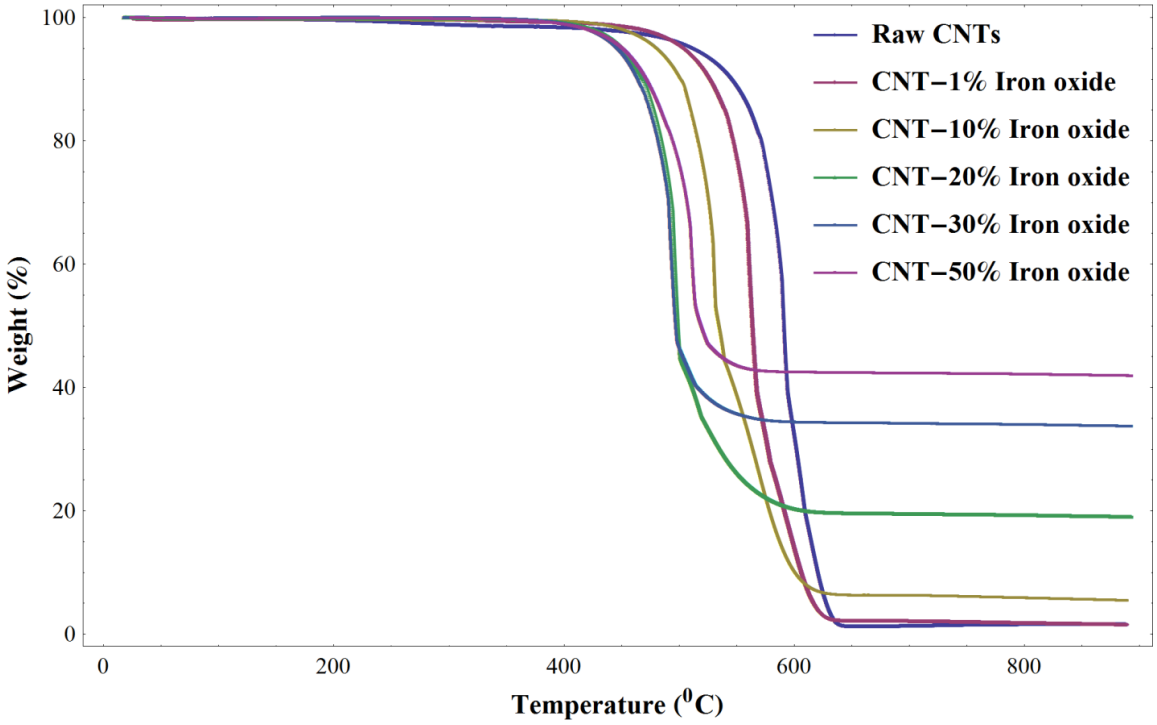


Figure 4-3: Thermogravimetric analysis (TGA) for raw CNTs and CNT-Fe_2O_3

4.3.3 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) of the raw and impregnated CNTs was performed to demonstrate the highly crystalline nature of the composites and confirm the attachment of iron oxide particles to the CNTs. The XRD patterns were recorded using an X-ray diffractometer equipped with a Cu Kα radiation source (40 kV, 20 mA) at a rate of 1.0°/min between 10-80° (2α). Fig. 4-4 displays the XRD patterns of the raw and doped CNTs. The XRD pattern of the raw CNTs presented two major characteristic peaks at 2θ ~ 27 and 44° that correspond to the hexagonal graphite lattice of multi-walled carbon

nanotubes. The XRD pattern of the impregnated CNTs presented new peaks in addition to the two obvious peaks associated with carbon nanotubes. The most significant Bragg diffraction peaks observed appeared at $2\theta = 34, 36, 42, 50, 54, 63$ and $65°$. These peaks correspond to the α-Fe_2O_3 nanoparticles [52]. These results demonstrate that the Fe_2O_3 particles were successfully attached to the CNTs.

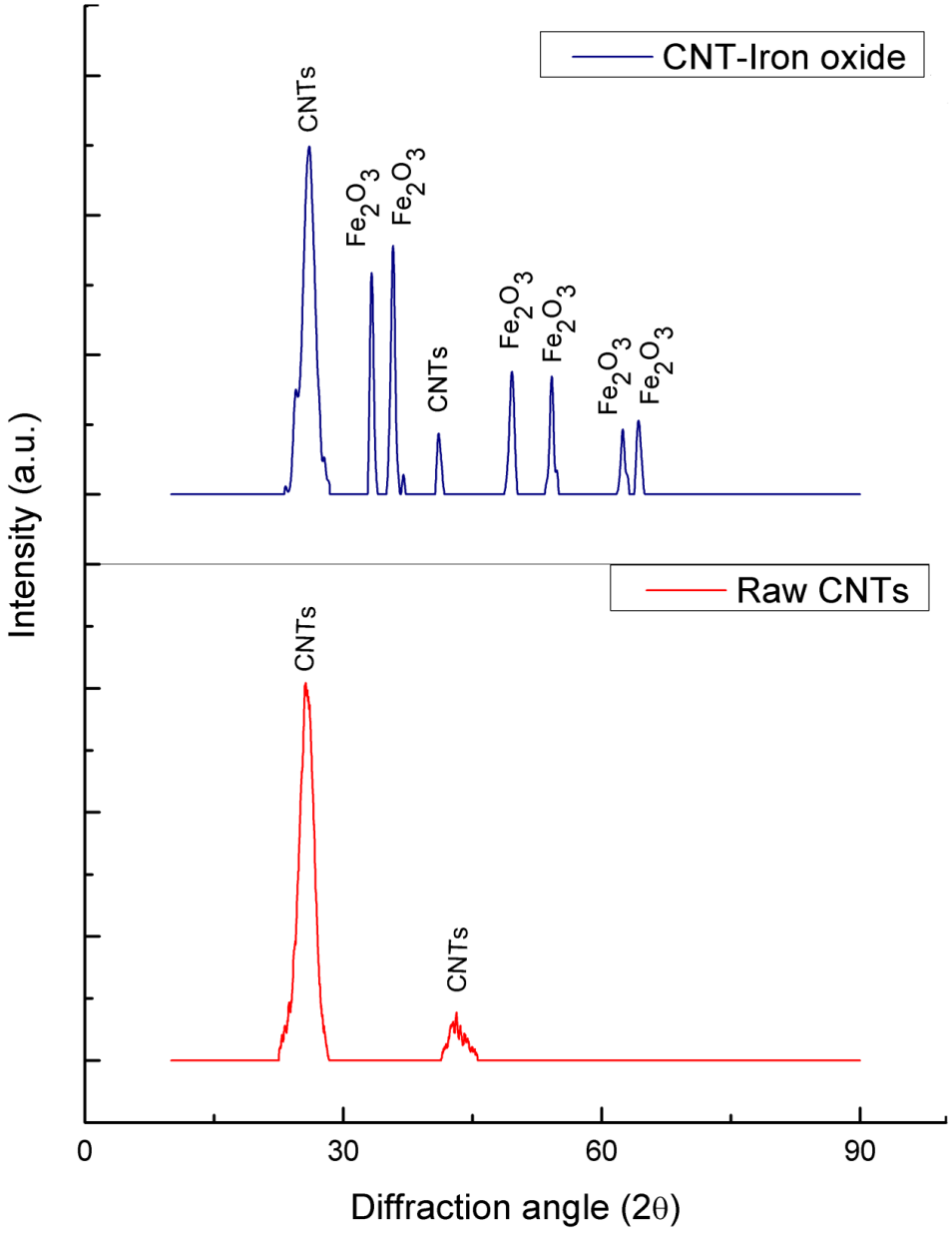


Figure 4-4: XRD patterns of the raw CNTs and CNT-Fe_2O_3

4.4 Membrane Preparation

Carbon nanotube doped iron oxide particles were uniaxially pressed into steel discs with a diameter of 27 mm under a pressure of 200 MPa. Compaction yielded a disc of approximately 27 x 3 mm containing 1, 10, 20, 30 and 50% iron oxide by mass. These discs were sintered in a horizontal tube furnace (MTI Corporation GSL-1700X) with a programmable temperature controller. Sintering was performed at temperature of 1350°C for 5 h under argon gas (300-400 mL/min) at a heating rate of 5°C/min. The membrane characteristics were analysed by SEM, EDS, XRD, porosity and contact angle measurements. A schematic of the membrane synthesis process is presented in Fig. 4-5.

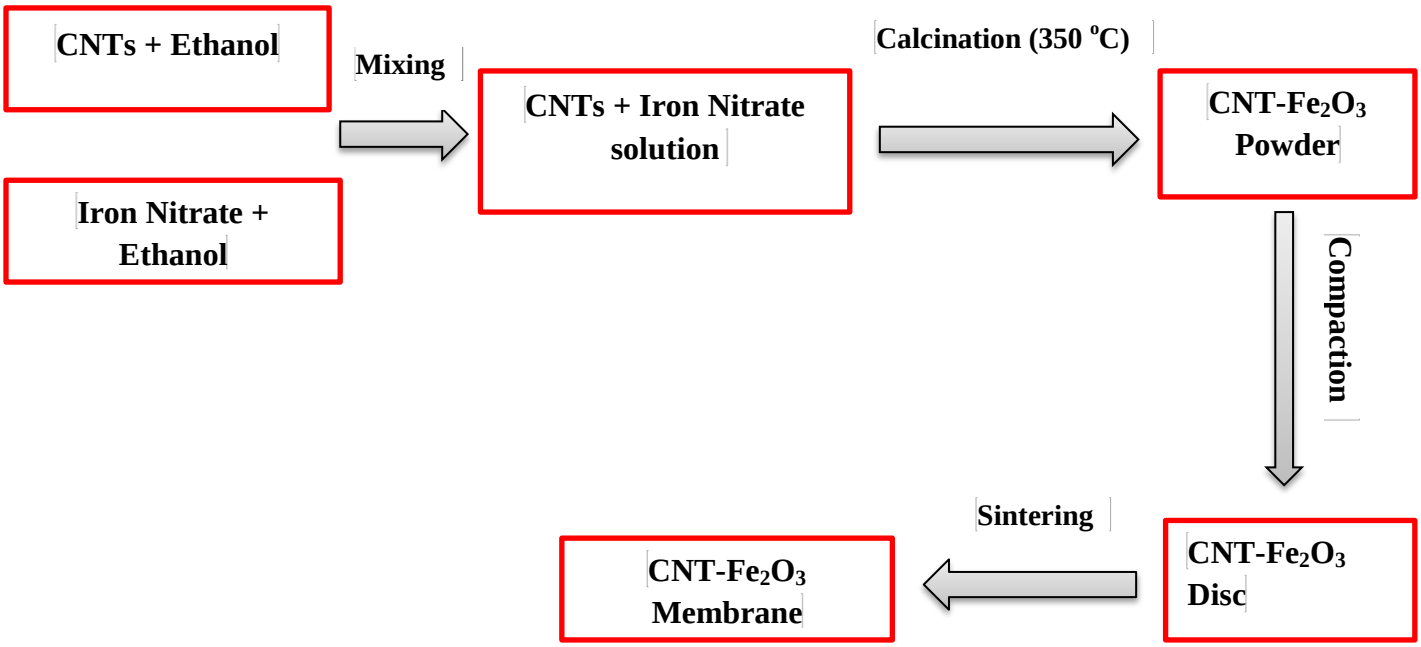
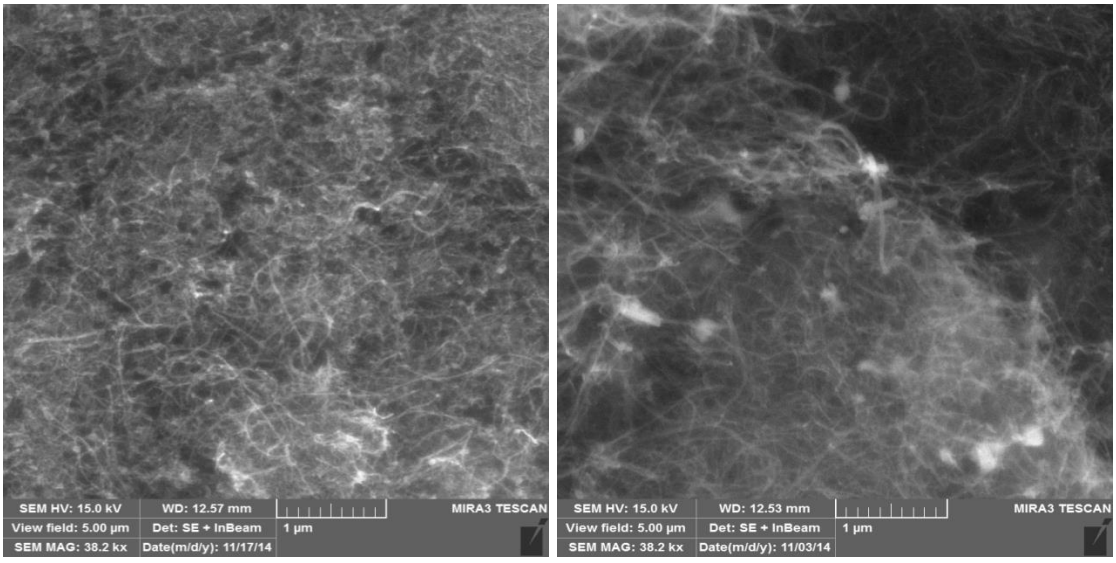


Figure 4-5: Flow chart of the iron doped CNT membrane synthesis

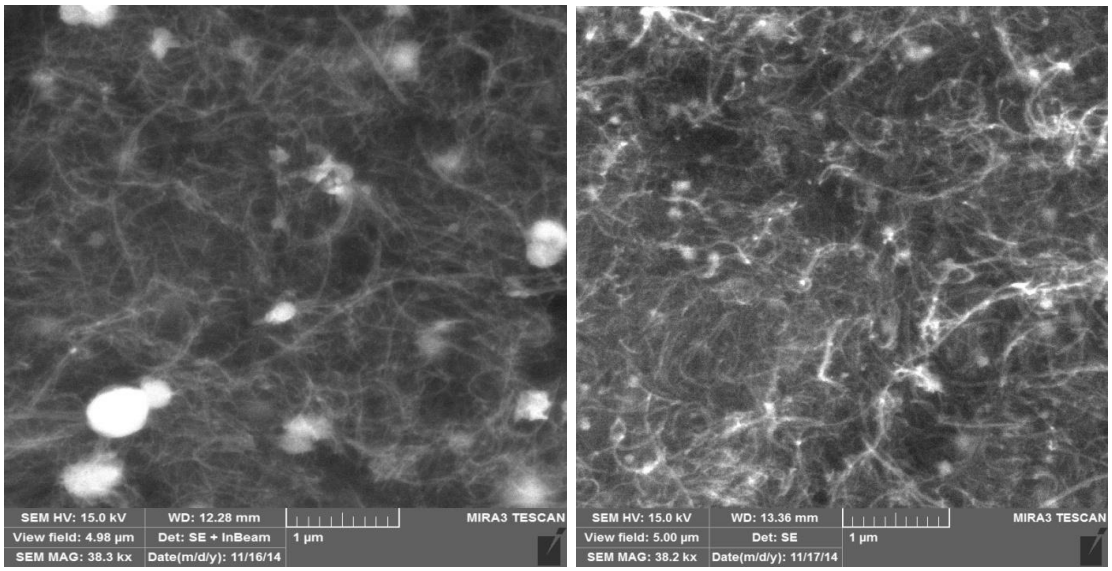
4.5 Membrane Characterization

4.5.1 Scanning Electron Microscopy (SEM)

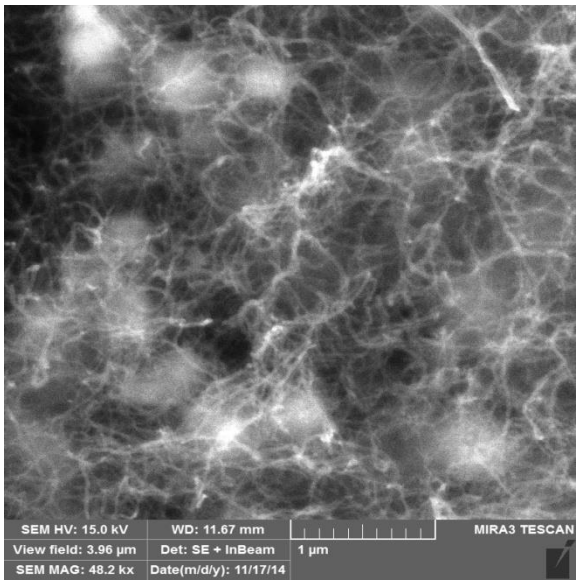
Scanning electron microscopy of the membranes was performed using a field emission scanning electron microscope (TESCAN MIRA 3 FEG-SEM). The membrane samples were sputtered with a 10 nm layer of platinum. Fig. 4-6 shows the SEM images of the sintered membranes with different iron oxide loadings. It can be seen that the Fe_2O_3 particles are well dispersed at lower particle loadings; however, some aggregation was observed when the amount of Fe_2O_3 loaded was higher. The membrane appears to be more porous, as confirmed by porosity measurements, when the iron oxide content is low. As the Fe_2O_3 loading is increased, the porosity is reduced due to the presence of Fe_2O_3 particles in the channels that exist among the CNTs.



(a) (b)



(c) (d)



(e)

Figure 4-6: SEM images of the CNT sintered membranes with (a) 1 (b) 10 (c) 20 (d) 30 and (e) 50% Fe_2O_3

4.5.2 Porosity Measurements

The porosity of the membranes was determined by the dry-wet method [32] using equation (1):

$$\text{Porosity} = \frac{W_2 - W_1}{\rho . V} \times 100\ \% \qquad (1)$$

Where w_1 (g) and w_2 (g) are the weight of the dry and wet membranes, respectively, ρ (g/cm^3) is the density of distilled water at room temperature, V (cm^3) is the volume of the membrane. The weight of the wet membrane was measured after being immersed in distilled water for 24 h. The wet membrane was then dried in an oven at 90 °C for 24 h before measuring its dry weight. In order to minimize the experimental error, the experiment was repeated three times and the average value is reported in Fig. 4-7.

The porosity of the membrane changes slightly as the iron oxide content is increased from 1 to 10%. However, a decrease in porosity was observed by increasing the iron oxide content from 10 to 30%. This may arise because as the iron oxide content is increased, the space between the CNTs becomes filled with the iron oxide particles, which attach to the CNTs, resulting in the porosity being reduced. After sintering, the particles attached to the CNT walls aggregate to hold the CNTs, and it is expected that the iron oxide particles will exist within the gaps between the CNTs. This leads to a reduction in porosity. Similar behaviour has been reported in the literature, whereby a decrease in flux is observed with filler loading [32, 53].

However, at higher iron oxide concentrations, the porosity again increases. This may be due to the formation of gaps at relatively high iron oxide loadings (50%) resulting from the agglomeration of iron oxide particles; these gaps allow water molecules to pass

through the membrane easily. A similar increase in porosity and flux at a high filler loading is also reported in the literature [54].

However, the change in porosity of the membrane observed by varying the iron oxide loading is very small. This indicates that the iron oxide content is not responsible for the significant change in the membrane porosity observed. The porosity depends predominantly on the CNT properties.

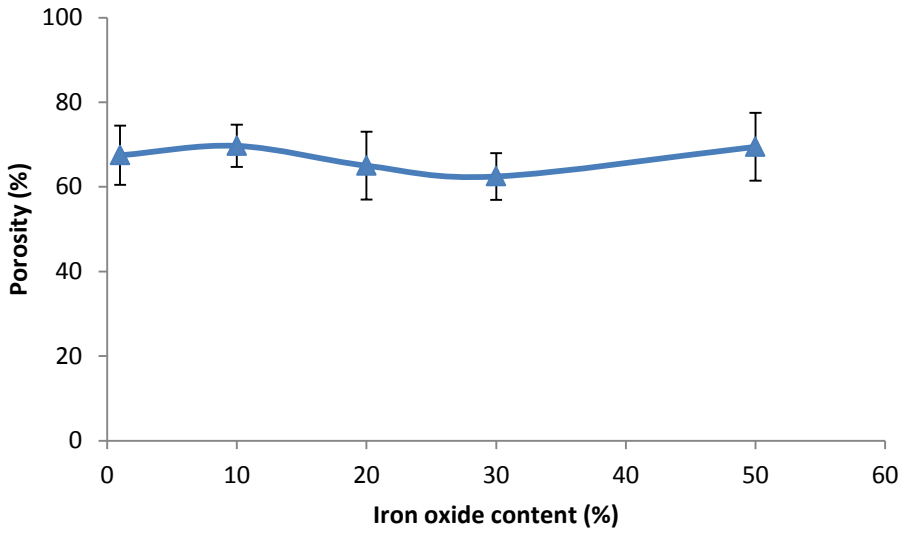


Figure 4-7: The varying membrane porosity with Fe_2O_3 content

4.5.3 Contact Angle Measurements

The contact angle gives an indication of the hydrophilicity and/or hydrophobicity of the membrane. The contact angle of the membrane surface was measured using a contact angle analyser (KYOWA, model DM-301). The measurements were carried out by placing a 5 µL water droplet onto the membrane surface. All experiments were repeated at five different sites, and the mean value reported.

It can be seen from Fig. 4-8 that the contact angle decreases with an increase in the iron oxide content in the membrane. This behaviour indicates that the hydrophilicity of the membrane increases as the iron oxide content increases. The hydrophilic nature of the membrane facilitates the rapid transport of water molecules through it, which results in the enhanced flux observed [24].

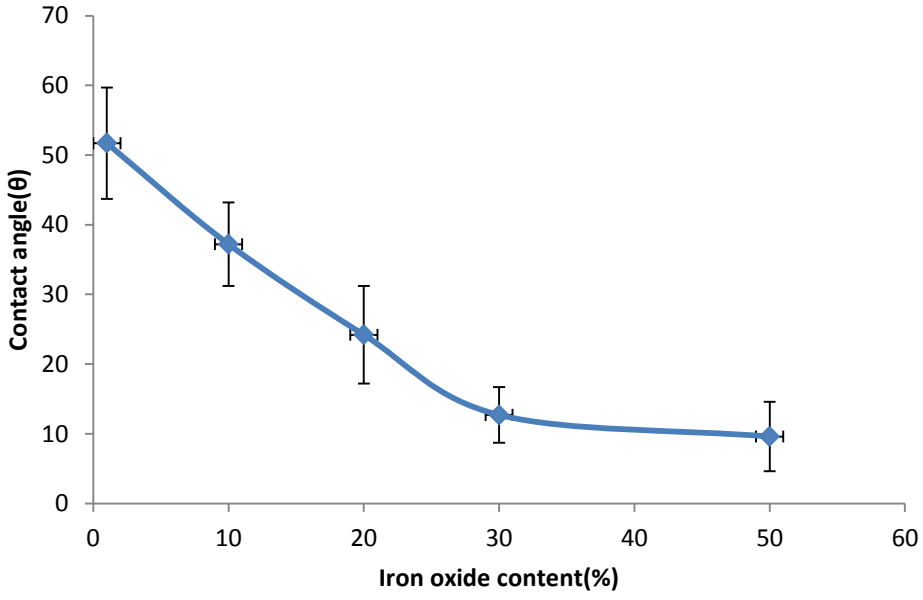


Figure 4-8: Contact angle of the membrane versus the iron oxide content

4.5.4 Diametral Compression Test

The mechanical strength of the CNT-Fe_2O_3 membranes was measured by applying the diametral compression test. The diametral compression test is often employed to predict the strength of porous materials. The membranes were pressed diametrally between two flat plates and the tensile strength of the sample was measured in the direction perpendicular to the load. The diametral stress (σ) can be calculated using equation (2) [55-56]:

$$\sigma = 2P/\pi D\, t \qquad (2)$$

Where t and D are the thickness and diameter of the membrane disc, respectively, and P is the load.

A schematic of the diametral compression is shown in Fig. 4-9 (a). The membrane samples had a 27 mm diameter and were 3 mm thick as shown in Fig. 4-9 (b). Samples were diametrally pressed between flat platens in an Instron universal testing machine with a crosshead speed of 0.01 mm/min. A fractured sample is shown in Fig. 4-9 (c). It can be observed that the sample fractured into two halves, which indicates that the sample underwent a tensile failure [55-56].

Fig. 4-10 shows the variation of compressive stress versus compressive strain. It was observed that the maximum compressive strength increases as the silver content in the membrane is increased up to 20% silver loading. This can be justified due to the improved dispersion of iron oxide particles that hold the CNTs together. As a result, the mechanical strength of the membrane increased. A maximum strength of 11.2 MPa was observed for the sample with a 20% Fe_2O_3 content. It was observed that the mechanical

strength of the membrane decreases with any further increase in the amount of Fe_2O_3 beyond 20%. This may be due to the agglomeration of iron oxide particles in the matrix, which leads to an increase in porosity. This increase in porosity resulted in a reduction of the mechanical strength of the membrane. Similar reductions in the mechanical strength associated with increased porosity at high filler loadings have been reported [57-58].

Figure 4-9: (a) Schematic of the diametral compression test and images of the CNT-Fe_2O_3 membrane (b) before and (c) after being subjected to a diametral compression test

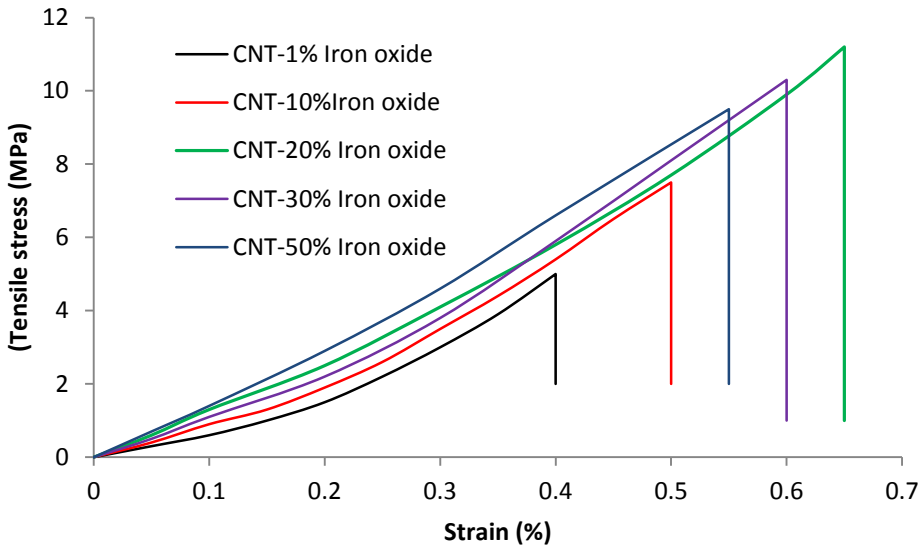


Figure 4-10: Diametral compression test curves

4.6 Water Flux Measurements

Water transport through the membrane depends predominantly on the hydrophilicity and porosity of the membrane. In general, the flux is higher for hydrophilic membrane surfaces with a high porosity. Water flux measurements were performed using a flow loop system as shown in Fig. 4-11. The pure water flux was determined by Eq. (3):

$$J = V/A.t \qquad (3)$$

where J (L. m^{-2}. h^{-1}) is the pure water flux, V (L) is the volume of permeate water, A (m^2) is the effective area of the membrane and t(h) is the time required for the permeate water to pass through the membrane (h). In our experiments, the surface area of the membrane was 5.7 cm^2.

The pure water flux was measured under different conditions as shown in Fig. 4-12 and 4-13. Initially, the water flux was measured at different transmembrane pressures, i.e.,

from 1 to 40 psi. Then the transmembrane pressure was maintained at 14 psi for 30 min and the water flux was measured. The same procedure was used to obtain the flux at different pressures. Each pressure was maintained for 10 min before recording a reading.

It can be seen from Fig. 4-12 that the flux increases as the iron oxide content increases. The higher flux of membranes with higher iron oxide concentrations can be justified on the basis of two mechanisms. First, at higher iron oxide content, the membrane surface is more hydrophilic, as confirmed by contact angle measurements. This leads to improved water transport through the membrane. Second, due to the aggregation of iron oxide particles at higher loading, large pores are formed among the CNTs and iron oxide particles; this facilitates a higher flux through the membrane. A slight reduction in the flux was observed with time for all membranes, as shown in Fig. 4-13. This may be due to the compaction of pores after water flow for long periods of time.

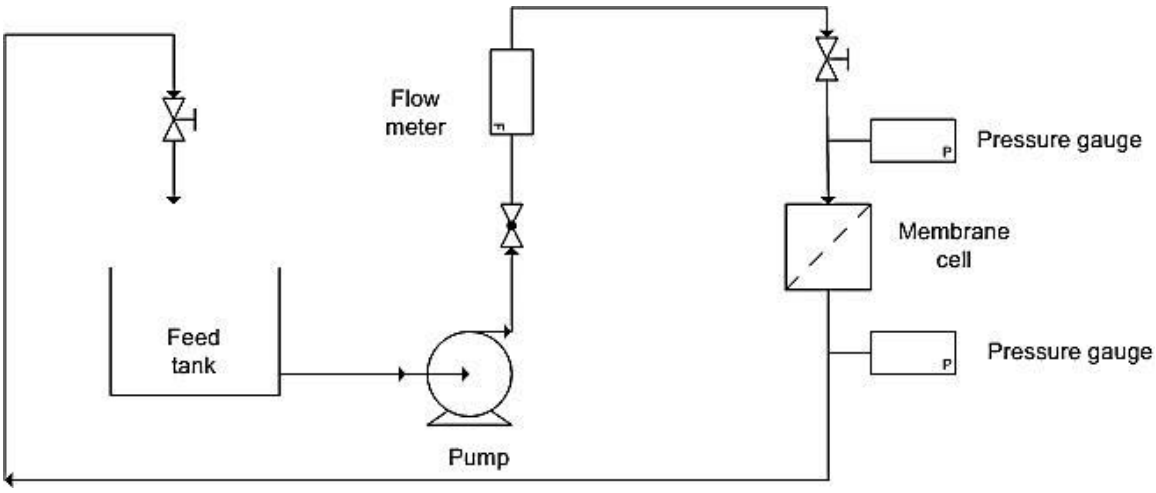


Figure 4-11: Schematic diagram of the flow loop system

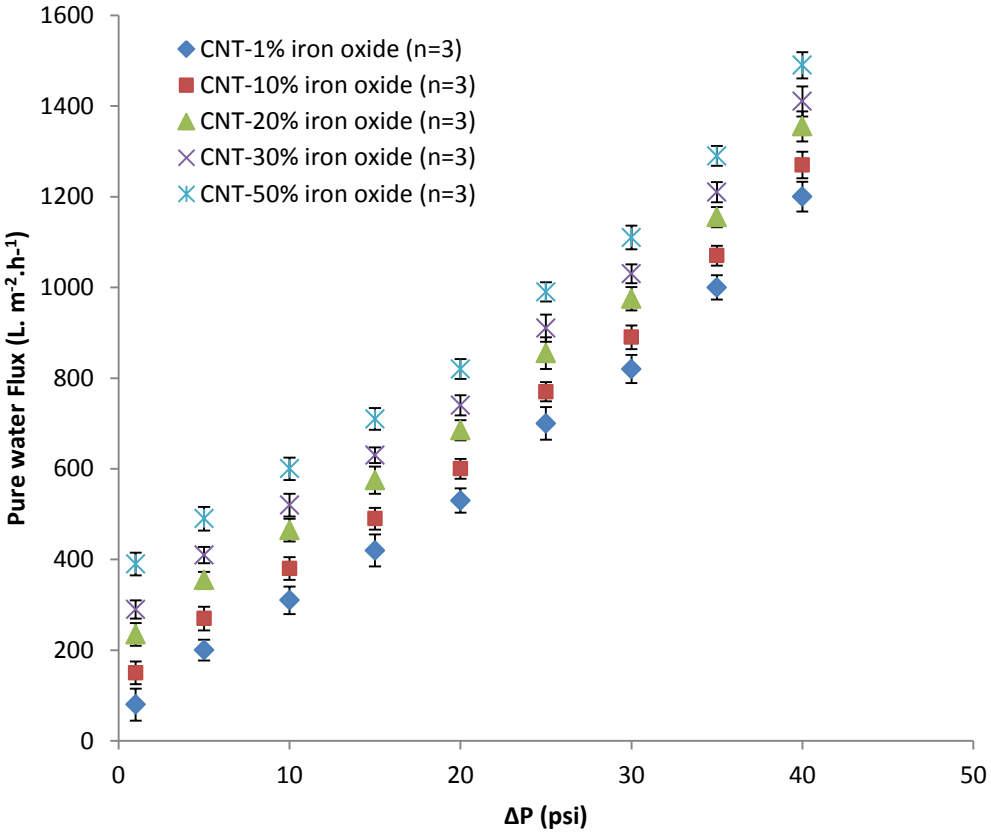


Figure 4-12: Effect of transmembrane pressure and iron oxide loading on pure water flux

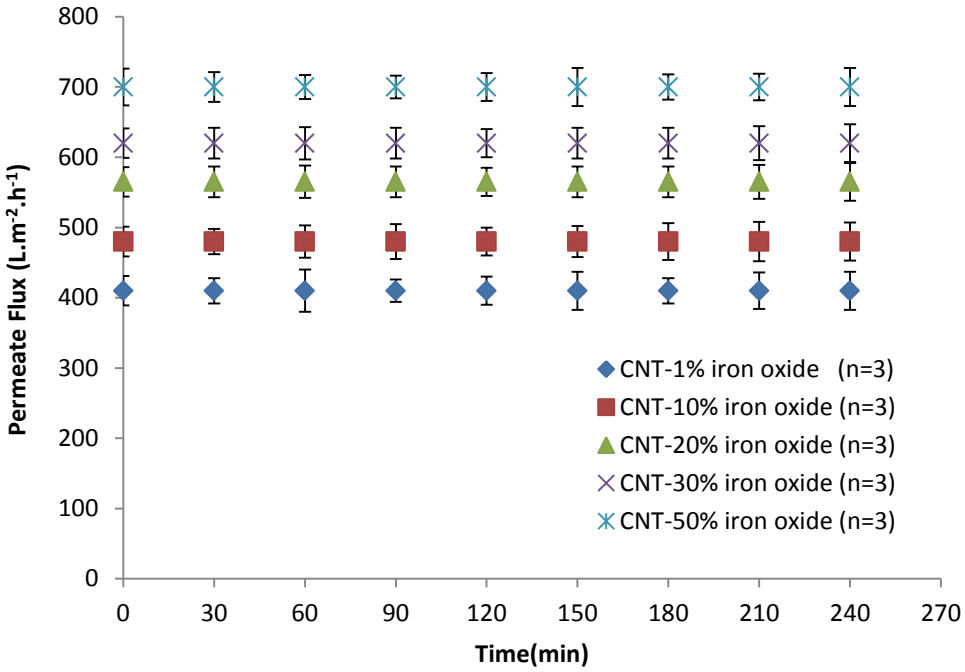


Figure 4-13: Effect of time on the pure water flux

4.7 Membrane Antifouling Properties

Extracellular polymeric substances (EPS) are one of the main causes of membrane fouling in water purification systems. Polysaccharides are major constituents in EPS, while sodium alginate is often used as a model for EPS [59-60].

The permeate flux and rejection rate of sodium alginate (SA) were determined to predict the antifouling behaviour of the membrane. A commercial sodium alginate with a reported molecular weight of 12–80 kDa was supplied by Sigma–Aldrich and employed in all experiments reported here. Alginate solutions with a concentration of 10 ppm were employed in each experiment; the concentration was measured using a total organic carbon (TOC) Shimadzu 5000 A analyser. The ionic strength of the solution was adjusted

by the addition of 20 mM NaCl and the pH was maintained at 7.8 by the addition of 1 mM $NaHCO_3$ buffer solution, as reported in the literature [61-63].

Alginate solutions were pumped through the flow loop system at a constant pressure of 14.7 psi, while permeated flux and concentrations were measured after equal time intervals. Results of the analysis are shown in Fig. 4-14 and 4-15. It can be observed from Fig. 4-14 that the permeate flux showed a minor decline after 90 min of operation. The maximum flux remained higher for membranes with an iron oxide content of 50%. This minor decline may be due to the smaller size of alginate, which may pass through the membrane pores with no significant effect on the flux. This suggests that at the initial stage of filtration, adsorption is the main phenomenon that explains the membrane fouling by alginate molecules. After a certain contact time (approximately 90 min in our case), cake development takes place on the membrane surface, which may cause a slight reduction in the permeate flux.

Sodium alginate rejection by the membrane was not significant until 0.5 h of operation, as shown in Fig. 4-14. This may be due to the smaller molecular size of alginate that requires sufficient time to deposit on the membrane surface and inside the pores. However, the rejection was observed to increase for all membrane types with time afterwards. A maximum rejection of sodium alginate of 90 and 88% was observed for membranes containing 10 and 1% iron oxide, respectively. This result is not surprising since the flux through membranes with low iron oxide content is smaller; hence, the longer contact time between the alginate molecules and membrane surface showed improved adsorption. Furthermore, a relatively good dispersion of iron oxide and CNTs

in these membranes contributes to the higher rejection of SA. The membrane with 50% iron oxide was still able to remove 57% alginate molecules after 3 h of operation.

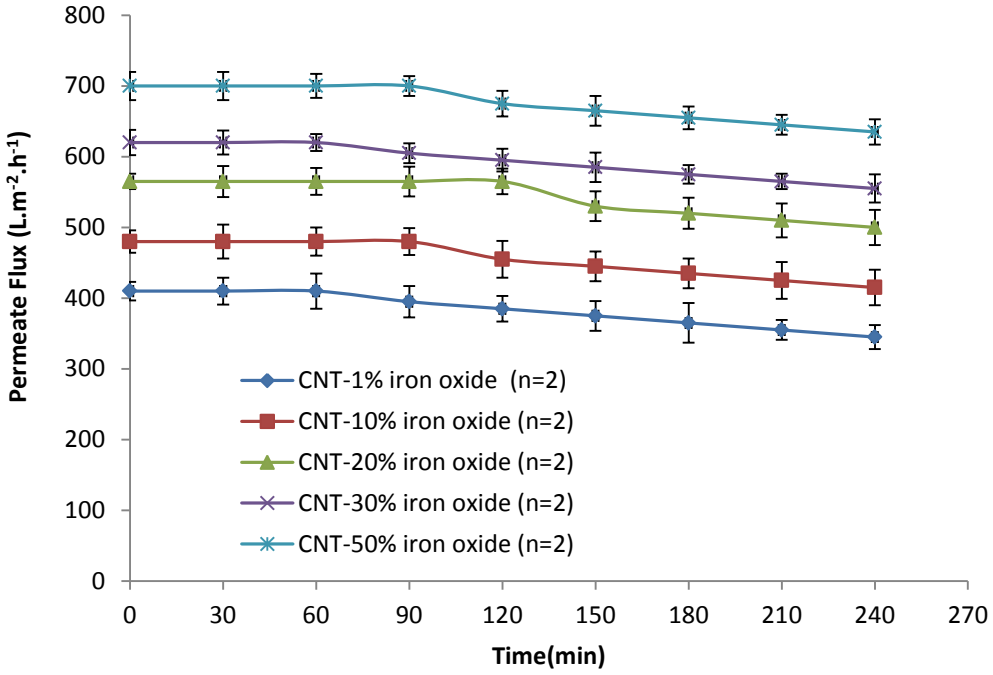


Figure 4-14: Permeate flux versus time

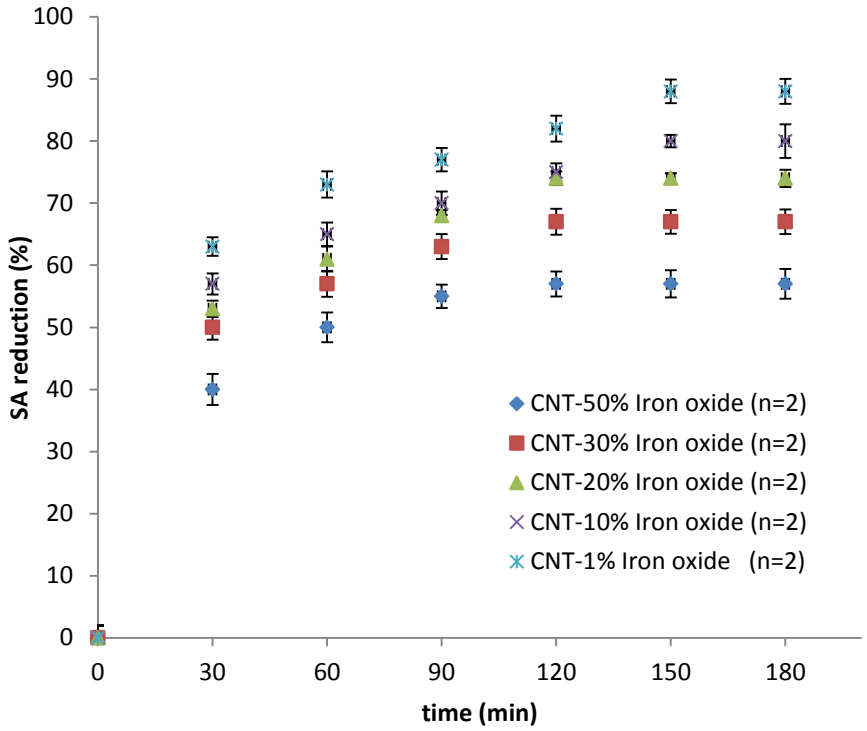


Figure 4-15: SA rejection versus time

4.8 Conclusions

Iron oxide-doped carbon nanotube membranes were successfully synthesized using a novel approach. The loading of iron oxide in the membrane was varied from 1 to 50 weight%. The produced membrane exhibited a high water flux and strong fouling resistance. The membrane characteristics were influenced remarkably by the iron oxide loading. The flux of pure water was observed to increase as the iron oxide content increased. A maximum flux of 1490 $L.m^{-2}.h^{-1}$ was observed for the membrane with a 50% iron oxide content. As the loading of iron oxide increased, it transformed the membrane from hydrophobic to hydrophilic, as confirmed by contact angle measurements. In addition, the membranes produced displayed a high mechanical strength. A maximum tensile strength of 11.2 MPa was observed for the membrane

containing 20% iron oxide. Irrespective of the iron oxide loading, all membranes prepared were effective in removing the SA from water. However, a maximum removal of 90 and 88% of SA was achieved for membranes with a 10 and 1% iron oxide content, respectively, after 3 h. A negligible reduction in the permeate flux was observed with time for all membranes.

Acknowledgements

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References

[1] X. Qu, P.J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res. 47 (2013) 3931–3946.

[2] S. Kar, R.C. Bindal, P.K. Tewari, Carbon nanotube membranes for desalination and water purification: Challenges and opportunities, Nano Today 7 (2012) 385-389.

[3] M. Cheryan. Ultrafiltration and Microfiltration Handbook. 2nd ed. CRC Press, 1998.

[4] M.M. Pendergast, E.M.V. Hoek. A review of water treatment membrane nanotechnologies, Energy Environ. Sci. 4 (2011) 1946-1971.

[5] R. Mallada, M. Menéndez, Inorganic Membranes: Synthesis, Characterization and Applications, 1st ed. Oxford: Elsevier, 2008.

[6] Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes, Carbon 4 (2003) 2787–2792.

[7] Ihsanullah, F. A. A. Khaldi, B. Abusharkh, M. Khaled, M.A. Atieh, M.S. Nasser, T. Laoui, S. Agarwal, I. Tyagi, V. K. Gupta, Adsorptive removal of Cadmium (II) ions from liquid phase using acid modified carbon-based adsorbents, J. Mol. Liq. 204 (2015) 248-254.

[8] Ihsanullah, F. A. A. Khaldi, B. A. Sharkh, A. M. Abulkibash, M. I. Qureshi, T. Laoui, M. A. Atieh, Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes, Desalin. water treat. (2015). doi: 1 0.1080/19443994.2015.1021847.

[9] C. Chen, J. Hu, D. Shao, J. Li, X. Wang, Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II), J. Hazard. Mater. 164 (2009) 923–928.

[10] Z.C.Di, Y.H. Li, Z.K. Laun, J. Liang, Adsorption of chromium(VI) ions from water by carbon nanotubes, Adsorpt. Sci. Technol. 22 (2004) 467–474.

[11] S.G.Wang, W.X. Gong, X.W. Liu, Y.W. Yao, B.Y. Gao, Q.Y. Yue, Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes, Sep. Purif. Technol. 58 (2007) 17–23.

[12] C. Chen, X. Wang X, Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes, Ind. Eng. Chem. Res. 45 (2006) 9144–9149.

[13] C.L. Chen, X.K. Wang, M. Nagatsu, Europium adsorption on multiwall carbon nanotube/iron oxide magnetic composite in the presence of polyacrylic acid, Environ. Sci. Technol. 43 (2009) 2362–2367.

[14] C.H. Chen, C.C. Huang, Hydrogen adsorption in defective carbon nanotubes, Sep. Purif. Technol. 65 (2009) 305–310.

[15] A. Gaur, M. Shim, Substrate-enhanced O_2 adsorption and complexity in the Raman G-band spectra of individual metallic carbon nanotubes, Phys. Rev. B. 78 (2008) 1254221-1254227.

[16] J. Goering, E. Kadossov, U. Burghaus, Adsorption kinetics of alcohols on single-wall carbon nanotubes: an ultrahigh vacuum surface chemistry study, J. Phys. Chem. C. 112 (2008) 10114–10124.

[17] H. Hyung, J.H. Kim, Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters, Environ. Sci. Technol. 42 (2008) 4416–4421.

[18] Ihsanullah, H.A. Asmaly, T.A. Saleh, T. Laoui, V.K. Gupta, M.A. Atieh, Enhanced adsorption of phenols from liquids by aluminum oxide/carbon nanotubes: Comprehensive study from synthesis to surface properties, J. Mol. Liq. 206 (2015) 176-182.

[19] H. A. Asmaly, B. Abussaud, Ihsanullah, T. A. Saleh, V. K. Gupta, M. A. Atieh, Ferric Oxide Nanoparticles decorated Carbon nanotubes and carbon nanofibers: from synthesis to Enhanced Removal of Phenol, J. Saudi Chem. Soc. 19 (2015) 511-520.

[20] B.S. Lalia, F. E. Ahmed, T. Shah, N. Hilal, R. Hashaikeh, Electrically conductive membranes based on carbon nanostructures for self-cleaning of biofouling, Desalination 360 (2015) 8–12.

[21] J.K. Holt, A. Noy, T. Huser, D. Eaglesham, O. Bakajin, Fabrication of a carbon Nanotube-cmbedded silicon nitride membrane for studies of nanometer-scale mass transport, Nano Lett. 4 (2004) 2245-2250.

[22] S.Li, G. Liao, Z. Liu, Y. Pan, Q. Wu, Y. Weng, X. Zhang ,Z. Yang, O.K.C. Tsuid,

Enhanced water flux in vertically aligned carbon nanotube arrays and polyethersulfone composite membranes, J. Mater. Chem. A. 2 (2014) 12171-12176.

[23] M. Majumder, N. Chopra, R. Andrews, B.J. Hinds, Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes, Nature 438 (2005) 44-44.

[24] J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes, Science 312 (2006) 1034-1037.

[25] P.S. Goh, A.F. Ismail , B.C. Ng, Carbon nanotubes for desalination: Performance evaluation and current hurdles, Desalination 308 (2013) 2–14.

[26] B.J. Hinds, N. Chopra, R. Andrews, V. Gavalas, L.G. Bachas, Aligned Multiwalled Carbon Nanotube Membranes, Science 303 (2004) 62-65.

[27] S.A. Miller, V.Y. Young, C.R. Martin, Electroosmotic Flow in Template-Prepared Carbon Nanotube Membranes, J. Am. Chem. Soc. 123 (2001) 12335-12342.

[28] W. Chengwei, L. Menke, P. Shanlin, L. Hulin, Well-aligned carbon nanotube array Membrane synthesized in porous alumina template by chemical vapor deposition, Chin. Sci. Bull. 45 (2000) 1373–1376.

[29] A. Srivastava, O.N. Srivastava, S. Talapatra, R. Vajtai, P.M. Ajayan, Carbon nanotube Filters, Nat. Mater. 3 (2004) 610–614.

[30] L.F. Dumee, K. Sears, J. Schütz, N. Finn, C. Huynh, S. Hawkins, M. Duke, S. Gray, Characterization and evaluation of carbon nanotube Bucky-Papermembranes for direct contact membrane distillation, J. Membr. Sci. 351 (2010) 36–43.

[31] R. Andrews, D. Jacques, A.M. Rao, F. Derbyshire, D. Qian, X. Fan, E.C. Dickey, J. Chen, Continuous production of aligned carbon nanotubes: A step closer to commercial realization, Chem. Phys. Lett. 303 (1999) 467–474.

[32] S. Majeed, D. Fierro, K. Buhr, J. Wind, B. Du, A.B.D. Fierro, V. Abetz, Multi-walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes, J. Membr. Sci. 403-404 (2012) 101– 109.

[33] D.L. Arockiasamy, J. Alam, M. Alhoshan, Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications, Appl. Water Sci. 3 (2013) 93–103.

[34] J. H. Choi, J. Jegal and W. N. Kim, Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes, J. Membr. Sci. 284 (2006) 406–415.

[35] P. Shah, C.N. Murthy, Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal, J. Membr. Sci. 437 (2013) 90–98.

[36] Ihsanullah, T. Laoui, A.M. Al-.Amer, A. B. Khalil, A. Abbas, M. Khraisheh, M. A. Atieh, Novel anti-microbial membrane for desalination pretreatment: A silver nanoparticle-doped carbon nanotube membrane, Desalination 376 (2015) 82-93.

[37] S.J. Oh, N. Kim, Y.T. Lee, Preparation and characterization of PVDF/TiO_2 organic– inorganic composite membranes for fouling resistance improvement, J. Membr. Sci. 345 (2009) 13–20.

[38] R.A. Damodar, S.J. You, H.H. Chou, Study the self cleaning, antibacterial and photo catalytic properties of TiO_2 entrapped PVDF membranes, J. Hazard. Mater. 72 (2009) 1321–1328.

[39] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized Al_2O_3-particle addition on PVDF ultrafiltration membrane performance, J. Membr. Sci. 276 (2006) 162–167.

[40] F. Liu, M.R.M. Abed, K. Li, Preparation and characterization of poly(vinylidene fluoride)(PVDF) based ultrafiltration membranes using nano γ-Al_2O_3, J. Membr. Sci. 366 (2011) 97–103.

[41] A. Bottino, G. Capannelli, A. Comite, Preparation and characterization of novel porous PVDF-ZrO_2 composite membranes, Desalination 146 (2002) 35–40.

[42] S.P. Nunes, K.V. Peinemann, K. Ohlrogge, A. Alpers, M. Keller, A.T.N Pires, Membranes of poly(ether imide) and nano dispersed silica, J. Membr. Sci. 157 (1999) 219–226.

[43] R. A. Gandhi, K. Palanikumar, B.K. Ragunath, J. P. Davim, Role of carbon nanotubes (CNTs) in improving wear properties of polypropylene (PP) in dry sliding condition, Mater. Design 48 (2013) 52–57.

[44] R. Theravalappil , P. Svoboda, J. Vilcakova, S. Poongavalappil, P. Slobodian, D. Svobodova, A comparative study on the electrical, thermal and mechanical properties of ethylene–octene copolymer based composites with carbon fillers, Mater. Design 60 (2014) 458–467.

[45] J. Huang, D. Rodrigue, The effect of carbon nanotube orientation and content on the mechanical properties of polypropylene based composites, Mater. Design 55 (2014) 653- 663.

[46] S.A.R. Hashmi, H. C. Prasad, R. Abishera, H. N. Bhargaw, A. Naik, Improved recovery stress in multi-walled-carbon-nanotubes reinforced polyurethane, Mater. Design 67 (2015) 492–500.

[47] L. Liu, D. Y. W. Di, H. Park, M. Son, H. G. Hurand H.Choi, Improved antifouling performance of polyethersulfone (PES) membrane via surface modification by CNTs bound polyelectrolyte multilayers, RSC Adv. 5 (2015) 7340-7348.

[48] F. Aviles, J.V. Cauich-Rodrıguez, L. M. Tah, A. M. Pat, R. V.Coronado, Evaluation of mild acid oxidation treatments for MWCNT functionalization, Carbon 4 7 (2009) 2970 –2975.

[49] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, Chemical oxidation of multiwalled carbon nanotubes, Carbon 4 6 (2008) 833 –840.

[50] Y. L. Luo, X. P. Wei, D. Cao, R. X. Bai, F. Xu, Y. S. Chen, Polystyrene-block-poly(tert-butyl methacrylate)/multiwall carbon nanotube ternary conducting polymer nanocomposites based on compatibilizers:Preparation, characterization and vapor sensing applications, Mater. Design 87 (2015) 149–156.

[51] H. Li, J. Fan, X. Geng, B. Li, C. Liang, H. Wang, Y. Li, Z. Qiao, J. Kang, Alumina powder assisted carbon nanotubes reinforced Mg matrix composites, Mater. Design 60 (2014) 637–642.

[52] R. Ramesh, K. Ashok, G.M. Bhalero, S. Ponnusamy, C. Muthamizhchelvan, Synthesis and properties of α-Fe_2O_3 nanorods, Cryst. Res. Technol. 45 (2010) 965 – 968.

[53] N. Scharnagl, H. Buschatz, Polyacrylonitrile (PAN) membranes for ultra- and microfiltration, Desalination 139 (2001) 191-198.

[54] H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite, J. Membr. Sci. 362 (2010) 374–383.

[55] F. Patel, M.A. Baig, T. Laoui, Processing of porous alumina substrate for multilayered ceramic filter, Desalin. Water Treat. 35 (2011) 33–38.

[56] P. Chen, H. Xie, F. Huang, T. Huang, Y. Ding, Deformation and failure of polymer bonded explosives under diametric compression test, Polym. Test. 25 (2006) 333–341.

[57] Y. Ma, F. Shi, J. Ma, M. Wu, J. Zhang, C. Gao, Effect of PEG additive on the morphology and performance of polysulfone ultrafiltration membranes, Desalination 272(1-3) (2011) 51–58.

[58] G.D. Vilakati, E.M.V. Hoek, B.B. Mamba, Probing the mechanical and thermal properties of polysulfone membranes modified with synthetic and natural polymer additives, Polym. Test. 34 (2014) 202–210.

[59] B.P. Frank, G. Belfort, Polysaccharides and sticky membrane surfaces: critical ionic effects, J. Membr. Sci. 212 (2003) 205–212.

[60] Y.Ye, P.L. Clech, V. Chen, A.G. Fane, B. Jefferson, Fouling mechanisms of alginate solutions as model extracellular polymeric substances, Desalination 175 (2005) 7–20.

[61] K.S. Katsoufidou, D.C. Sioutopoulos, S.G. Yiantsios, A.J. Karabelas, UF membrane fouling by mixtures of humic acids and sodium alginate: Fouling mechanisms and reversibility, Desalination 264 (2010) 220-227.

[62] E. Aoustin, A.I. Schaefer, A.G. Fane, T.D. Waite, Ultrafiltration of natural organic matter, Sep. Purif. Technol. 22-23 (2001) 63–78.

[63] K. Katsoufidou, S.G. Yiantsios, A.J. Karabelas, Experimental study of ultrafiltration membrane fouling by sodium alginate and flux recovery by backwashing, J. Membr. Sci. 300 (2007) 137–146.

CHAPTER 5

NOVEL ANTI-MICROBIAL MEMBRANE FOR DESALINATION PRETREATMENT: A SILVER NANOPARTICLE-DOPED CARBON NANOTUBE MEMBRANE

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Abstract

A novel approach was used to synthesize a silver doped-CNT membrane, with the aim of fully utilizing the anti-toxic properties of CNTs and silver. No binder was used for the synthesis of the membrane; instead, silver particles served as a binding material for the CNTs after sintering at a high temperature. In the first step, CNTs were impregnated with different loads of silver (1, 10 and 20 wt%) via a wet chemistry technique. Impregnated CNTs were then compacted at 200 MPa and sintered at 800 ^{o}C for 3 hours to form a compact disc. The powder materials were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD) and thermogravimetric analysis (TGA), while the membranes were characterized by measuring their porosity, contact angle, diametrical compression test, pure water flux and antibacterial properties. The affinity of the membranes to biofouling was studied using Escherichia coli (E. coli). The produced membrane showed a high water flux and exhibited strong antibacterial properties. These membranes would be advantageous in a continuous filtration system for the removal of different contaminants from water via desalination, adsorption and sieving. All of the membranes with different loads of silver were able to remove/kill 100% of the bacteria tested; however, the CNT membrane with 10% silver showed a superior performance to the others. All of the bacteria were removed/killed by the membrane with 10% silver loading after the suspension had passed for only 60 min. The produced membrane has the potential to be employed in real water treatments system for the removal of a number of contaminants from wastewater.

5.1 Introduction

High quality water is not only important to human health but also serves as an essential feedstock for various industries, including petrochemicals, oil and gas, pharmaceuticals and food. Our current water supply faces massive challenges, both old and new. Worldwide, some 780 million people still lack access to safe drinking water (WHO, 2012) [1]. Water use has been growing at more than twice the rate of population growth in the last century. As per a report from the United Nations (UN), by 2025, 1800 million people will be facing absolute water scarcity, and two-thirds of the world population could be under water stress conditions [1, 2].

The available supplies of water are depleting due to increased population growth and competing demands from industrial and domestic users. Hence, alternative sources of water need to be explored. The possible alternative sources include: industrial wastewater, storm water and seawater. Water reuse, recycling, and recovery have proven to be successful and effective in creating a new and reliable water supply, while not compromising public health. Membrane filtration is considered to be among the most promising and widely used processes for the purification of wastewater, seawater and brackish water [1-3].

Nanotechnology has great potential in water treatment for the removal of a number of contaminants from water. Various nanostructured materials, such as zeolites, metal/metal-oxide nanoparticles, dendrimers and carbon nanotubes (CNTs), have been widely employed in water purification. Among these, CNTs are considered to be a versatile and unique material due to their extraordinary electrical, thermal and mechanical properties. CNTs have been extensively employed for the removal of various

contaminants from water, including heavy metal ions [4- 18], hydrogen and oxygen molecules [19-21] and organic chemicals [22-25].

CNTs have also been employed for the synthesis of novel membranes with extraordinary properties for water purification [26-28]. The higher transport of molecules is possible through the smooth and friction-less graphitic walls of CNTs [27-28]. CNTs were used as direct filter and appealing membrane fillers to enhance thermal, mechanical and electrical properties of polymeric composite materials [29-43]. The permeate flux through CNTs has been estimated to be 3-4 orders of magnitude faster than predicted by the Hagen-Poiseuille equation [30-33].

In the literature, different approaches have been reported by researchers for the synthesis of CNT-based membranes. These include template-assisted open-ended CNT membranes [32]; aligned-array outer-wall CNT membranes [33]; multi-stacked membranes of aligned CNT bundles [37]; vertically aligned open-ended CNTs surrounded by an inert polymer or ceramic matrix [30]; membranes composed of nanotubes in the form of a thin mat, also known as buckypaper membranes [34-36]; and mixed-matrix membranes [38-39]. Among these categories, the mixed-matrix membrane has gained considerable attention due to its ease of synthesis and broad applications. Different nanoparticles, such as TiO_2 [44–46], Al_2O_3 [47–48], ZrO_2 [49], and SiO_2 [50], can be employed as filler materials for the synthesis of mixed-matrix membranes with improved performance. The anti-bacterial potential of different metals has been reported by various researchers. However, silver nanoparticles (AgNPs) are currently the most effective and well-known antibacterial agents. Studies have confirmed that silver nanoparticles can deactivate microorganisms during water filtration. The antimicrobial effects of AgNPs can be

attributed to their capacity to damage cell protein and DNA, to interrupt electron transport chains and disturb cell membrane functions [51-52].

Membranes are very effective in water purification because of their potential to remove inorganic compounds, organic pollutants, and microorganisms and to limit microbial regrowth. However, biofouling is a serious problem associated with membrane separation [53-54]. Membrane biofouling is initiated by the irreversible adhesion of one or more bacteria to the membrane surface, followed by the growth and multiplication of the sessile cells at the expense of feed water nutrients. The adverse effects of biofouling include increased energy requirements to overcome biofilm resistance, flux decline, bio-deterioration and/or biodegradation of the membrane material; to increase in the solute concentration polarization; and to establish concentrated populations of human pathogens on membrane surfaces. Biofouling prevention/control is a serious issue for many membrane applications. In this respect, more effective techniques are needed to prevent/control the formation of biofilms on the membrane surface [55-56, 58, 60].

This paper describes a novel synthesis concept of a CNT metal oxide membrane that is composed of dispersed CNTs and silver nanoparticles. In the first step, CNTs were impregnated with different amounts of silver (1, 10 and 20%) via a wet chemistry technique. Impregnated CNTs were then compacted and sintered to form a compact disc. The effect of the silver amount, compaction force and sintering temperature were studied on the membrane properties. Powder materials were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and thermogravimetric analysis (TGA), while prepared membranes were analyzed

by measuring their porosity, contact angle, mechanical strength and water permeate flux. The affinity of membranes to biofouling was studied using E. coli.

5.2 Experimental Details

5.2.1 Materials

Multi-walled carbon naontubes used in this study were supplied by Chengdu Organic Chemicals Co. Ltd. (China). The purity of CNTs was > 95% while their length and outer diameter of CNTs were 1-10 μm and 10-20nm, respectively. Silver Nitrate ($AgNO_3$, reagent grade, Sigma Aldrich, purity ≥ 99%) was used as salt for the silver.

The silver nanoparticles were impregnated on the surface of the CNTs by a wet impregnation method. For example, for 1% silver loading, 0.315 g of pure $AgNO_3$ was dissolved in 500 mL of ethanol (98% purity). An amount, 19.8 g, of CNTs was also dissolved in 600 mL of absolute ethanol. Both solutions were sonicated for 1 hour separately and then mixed together. The resultant mixture was again sonicated for 2 hours at room temperature. The aim of ultrasonication was to have a complete and homogeneous wetting of the particles during impregnation and to decrease the possibility of agglomeration due to the formation of clumps of liquid. The mixture was then kept in an oven to evaporate the ethanol. The residue was then calcinated for 4 hours at 350 ^oC in a furnace under nitrogen to impregnate the CNTs with silver. This process leads to homogenously dispersed silver nanoparticles in a CNT matrix and the attachment of silver to the CNTs. Similarly, the CNTs were doped with different loads of silver, i.e., 10 and 20 %.

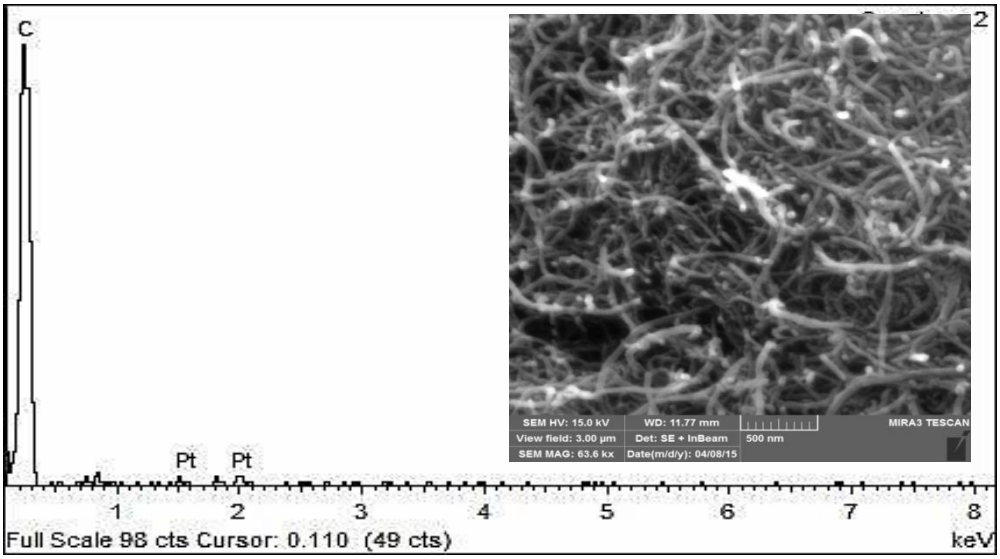
5.3 Characterization Techniques

Various analytical techniques were used to observe the characteristics of the raw and modified adsorbents. SEM studies were performed using field emission scanning electron microscope (TESCAN MIRA 3 FEG-SEM). TGA was performed using thermogravimetric analyzer (K.U. Leuven SDT, Q600) at a heating rate of 10°C/min in air. The XRD patterns were recorded using an X-ray diffractometer, equipped with Cu KR radiation (40 kV, 20 mA) at a rate of 1.0°/min over the range of 10-80° (2α). The contact angle of the membrane surface was measured using a contact angle analyzer (KYOWA, model DM-301). Diametral compression test was performed using Instron universal testing machine.

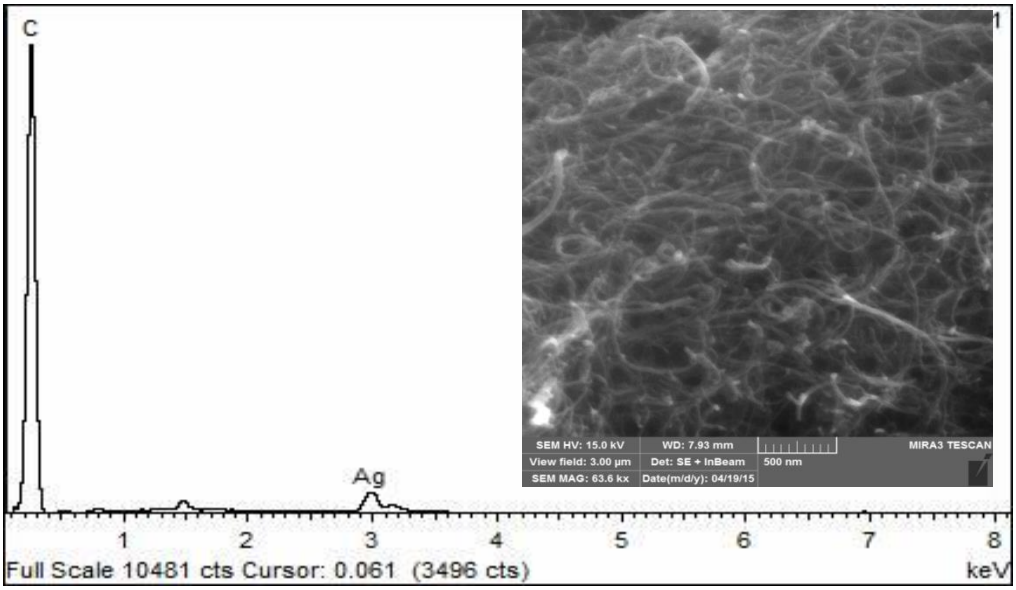
5.4 Characterization of Raw and Impregnated CNTs

5.4.1 SEM and EDS Analysis

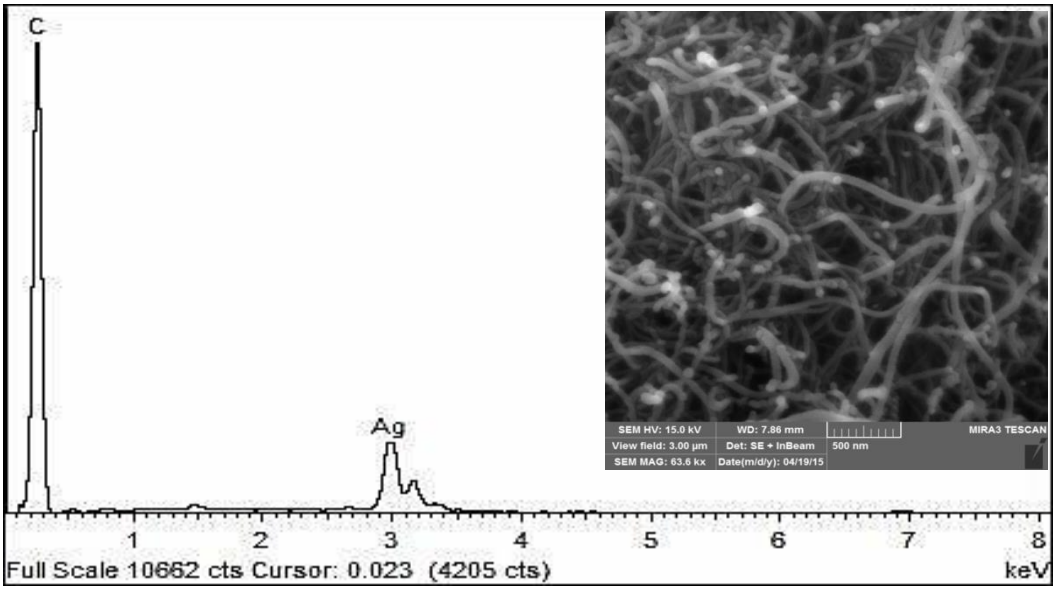
Fig. 5-1 displays the SEM images of CNTs and CNT-Ag. The white spots in the SEM image of CNT-Ag are the silver particles, as confirmed by an EDS analysis. The outcome of the analysis is the EDS spectrum in Figure 5-1. A back-scattering FE-SEM image of the CNT-Ag was taken to verify the presence of nanoparticle ions on the surfaces of the CNTs, as shown in Fig. 5-1. The distribution and agglomeration of the Ag nanoparticles was also observed. There are formations of white crystal structures of Ag nanoparticles with small sizes and irregular shapes. The Ag nanoparticles spread widely on the surfaces of the CNTs, forming very small crystal particles.



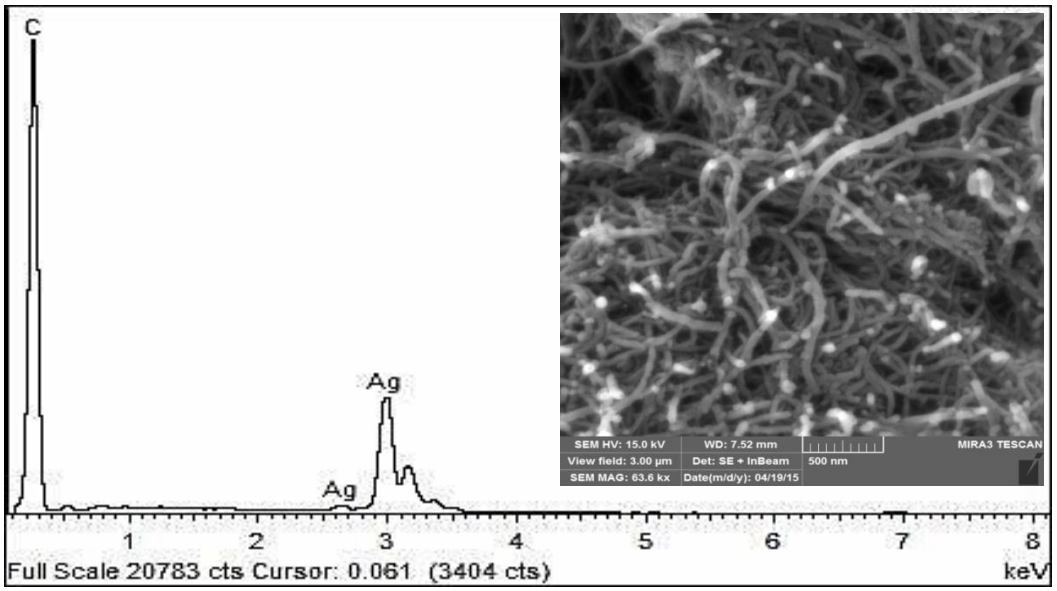
(a) Raw CNTs



(b) 1 % CNT-Ag



(c) 10 % CNT-Ag



(d) 20 % CNT-Ag

Figure 5-1: SEM images and EDS analysis of (a) Raw CNTs and (b, c and d) CNTs impregnated with silver nanoparticles

5.4.2 Thermal Degradation Analysis

The thermal degradation of the raw and impregnated CNTs was studied using TGA. Fig. 5-2 shows the TGA curves for the CNTs and CNT-Ag with different silver loads under air with a heating rate of 10 ^{o}C/min. The initial degradation temperature of the CNTs was found to be 550 °C, while degradation completes were observed at approximately 640°C. For CNT-Ag-1%, the initial oxidation temperatures started at 400°C and were completed at approximately 520°C. As the loading of Ag increases in the CNTs, the initial and final degradation temperatures were observed to decrease. The initial and final degradation temperatures of CNT-Ag-20% were recorded to be 300°C and 450°C, respectively. It was confirmed that presence of silver nanoparticles reduces the initial and final degradation temperature of CNTs. The sample weight was reduced to almost percentage loading of Ag at 900^{o}C. This is because all of the carbonaceous materials were removed and a small amount of metal was left behind.

5.4.3 X-Ray Diffraction (XRD)

Fig. 5-3 shows the XRD pattern for the doped CNTs. Two of the characteristic peaks of the CNTs were observed at a 2θ of 27 and 43^{o}, while other characteristic peaks were found at a 2θ of 40, 46, 68, 78, and 82^{o}, which corresponds to silver. These results revealed that the silver particles were successfully attached to the CNTs.

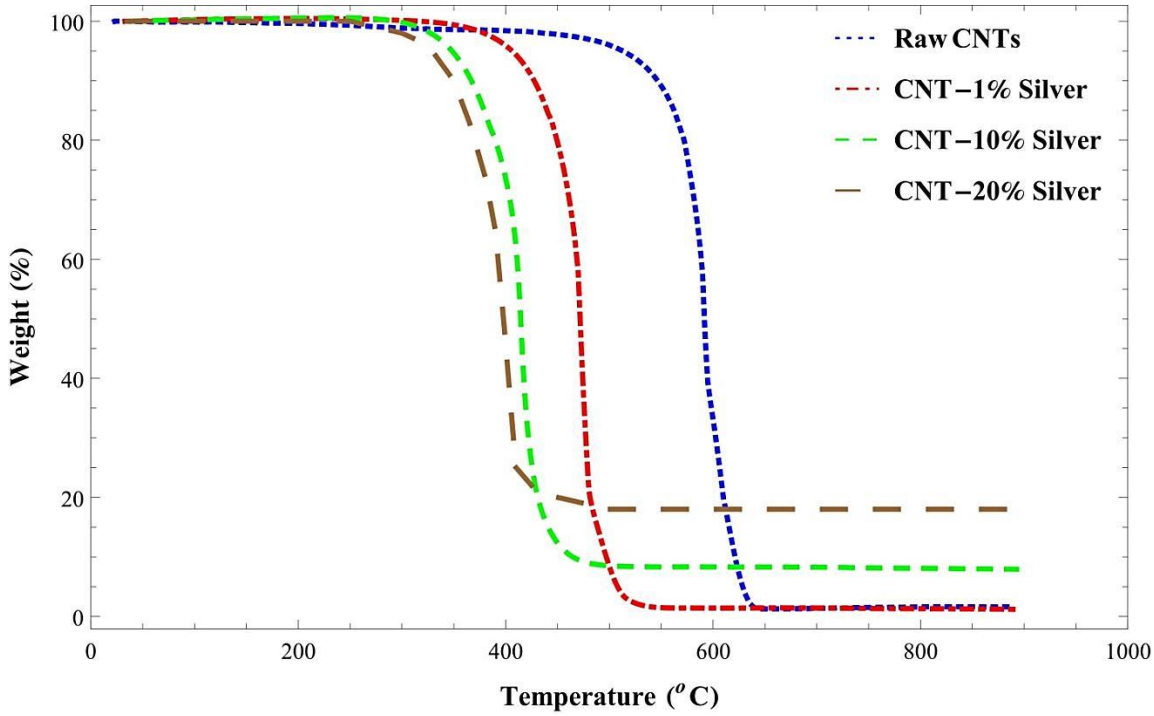


Figure 5-2: Thermogravimetric analysis (TGA) for raw CNTs and CNT-Ag

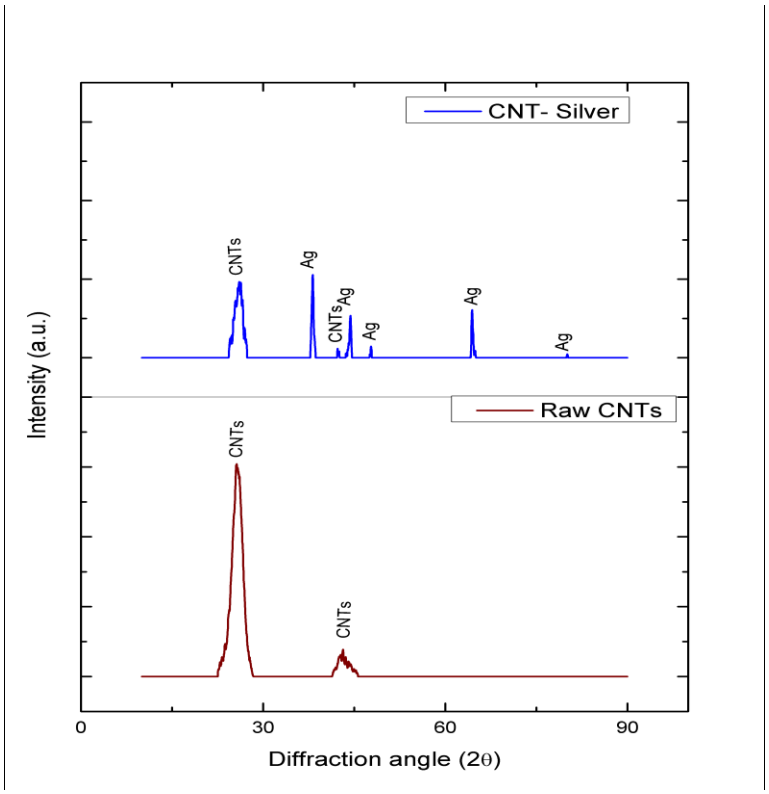


Figure 5-3: XRD pattern for raw CNTs and CNT-Ag

5.5 Membrane Preparation

CNTs doped with silver particles were uniaxially pressed in steel dies with 27-mm diameters under 200 MPa. Compaction yielded a disc of φ 27 mm x 3 mm containing 1, 10 or 20% of silver by mass. These discs were sintered in a horizontal tube furnace (MTI Corporation GSL- 1700X) with a programmable temperature controller. Sintering was performed at a temperature of 800 °C for 5 hours with a heating rate of 10 ^{o}C/min. The characteristics of the membranes were analyzed by SEM, EDS, porosity, diametrical compression test, pure water permeate flux and contact angle measurement. A schematic of the membrane synthesis process is presented in Fig. 5-4.

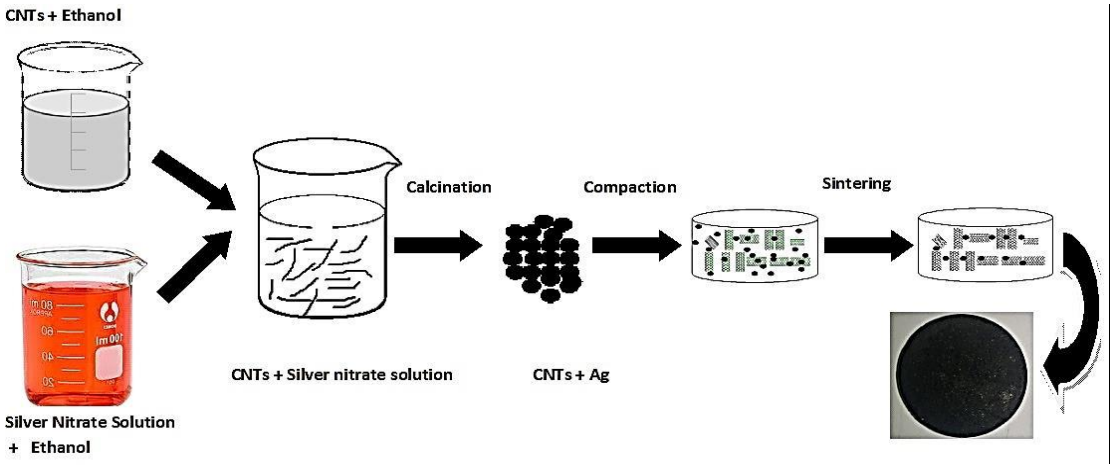
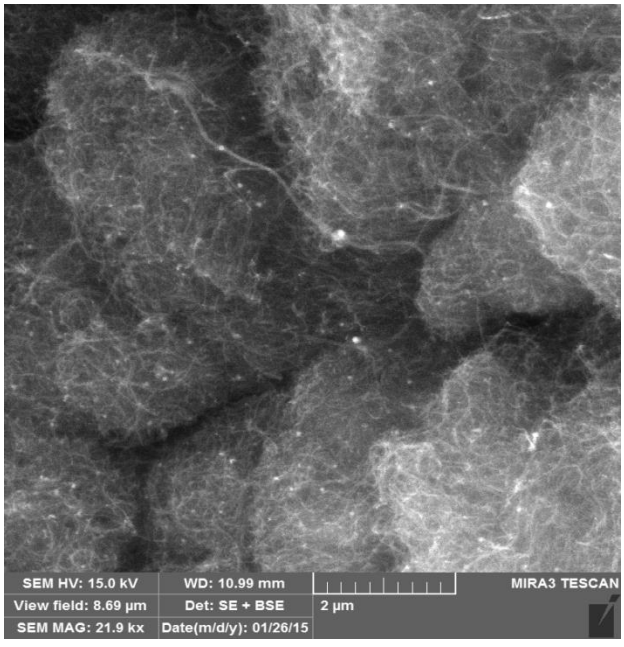


Figure 5-4: Schematic of silver doped CNTs membrane synthesis process

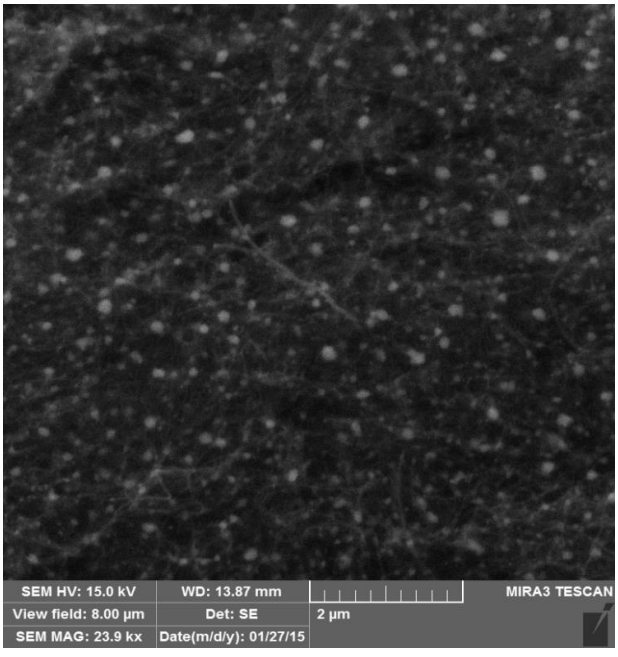
5.6 Membrane Characterization

5.6.1 Scanning Electron Microscopy (SEM)

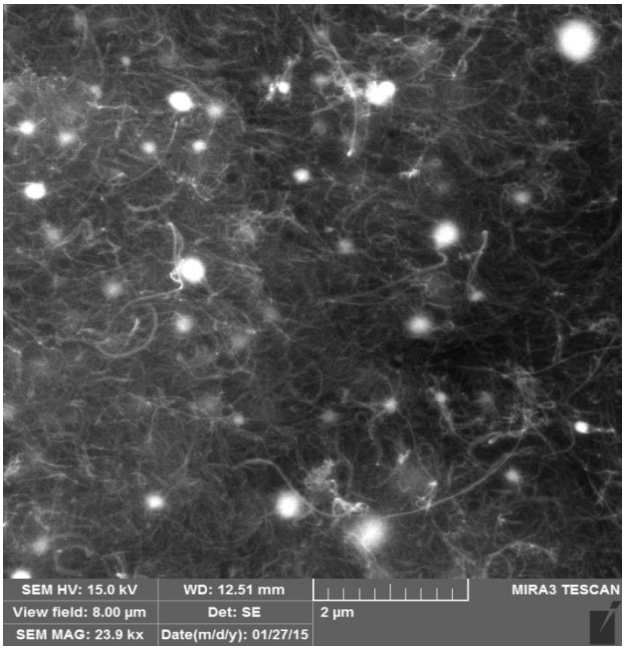
SEM for the membrane was performed using a Field Emission Scanning Electron Microscope (TESCAN MIRA 3 FEG-SEM). The membrane samples were sputtered with a 10-nm layer of platinum. Fig. 5-5 shows SEM images of the sintered membrane with different loads of silver. It can be seen that silver particles are disparate at lower loading levels; however, some aggregation was observed when the amount of silver was larger. The membrane seemed to be more porous, as confirmed by the porosity measurement, when the silver content was low. As the silver loading increased, the porosity was reduced slightly due the presence of the silver particles in the channels that exist among the CNTs.



(a)



(b)



(c)

Figure 5-5: SEM images of the CNT sintered membranes with (a) 1 (b) 10 and (c) 20 % silver

5.6.2 Porosity Measurement

Porosity of the membranes was measured by the dry-wet method [57], using the equations (1-2):

$$\text{Porosity} = \frac{W_2 - W_1}{\rho . V} \; x \; 100 \; \% \qquad (1)$$

$$\text{Volume} = \frac{\pi}{4} D^2.h \qquad (2)$$

Where w_1 (g) and w_2 (g) are the weights of dry and wet membranes, respectively, ρ (g/cm^3) is the density of distilled water at room temperature, V (cm^3) is the volume of the membrane, D (cm^3) is the diameter of the membrane, and h (cm) is the height/thickness of the membrane. The weight of wet membrane was measured after dipping into distilled water for 24 h. Then, the wet membrane was dried in the oven at 90 °C for 24 h before

measuring its dry weight. In order to minimize the experimental error, the experiment was repeated three times and the average value was reported in Fig. 5-6.

The porosity of the membrane increased slightly with the increase in silver content from 1 to 10 %. This might be due to a more hydrophilic surface of the membrane at 10% Ag loading. However, a slight decrease in porosity was observed when increasing silver from 10 to 20%. This might be because, with the increase in silver content, the spaces between CNTs were most likely to be covered by silver particles and hence the porosity was slightly reduced. However, the change in porosity of the membrane was very small by varying the silver loading. This indicated that the silver content did not bring about a major change in porosity of the membrane. The porosity value mainly depends on the CNT properties.

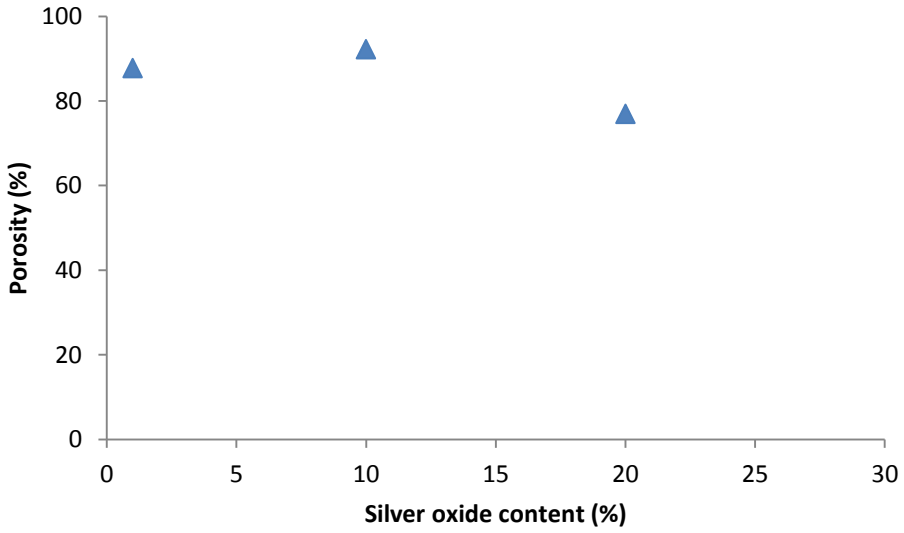


Figure 5-6: Porosity of membrane with different silver content

5.6.3 Contact Angle Measurements

The contact angle is an indication of the hydrophilicity of the membrane. The contact angle of the membrane surface was measured using a contact angle analyzer (KYOWA, model DM-301). The measurement was carried out by dropping a 1-µL droplet of water on the membrane surface.

The experiments were repeated at five different areas, and the mean values were reported. It can be seen from Fig. 5-7 that the contact angle decreases with increase in the silver content in the membrane. This behavior shows an increase in the hydrophilicity of the membrane with the increase in silver content. The hydrophilic nature of the membrane facilitates the rapid transport of water molecules through it and thus enhanced the permeate flux.

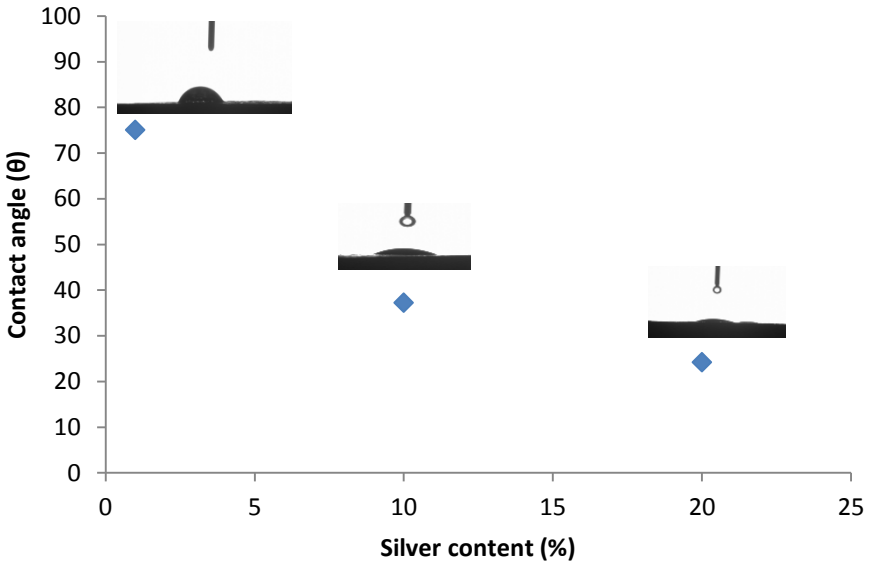


Figure 5-7: Contact angle of membrane versus silver content

5.6.4 Diametral Compression Test

The mechanical strength of CNTs-Ag membranes was measured by the diametral compression test. The diametral compression test is frequently used to measure the strength of porous materials. It measures the tensile strength of the sample in the direction perpendicular to the loading direction. In this test, the membranes were diametrally pressed between two flat plates.

The diametral stress is then calculated as follows [58-59]:

$$\sigma = \frac{2P}{\pi D\, t} \qquad (3)$$

where P is the load, D is the diameter and t is the thickness of the membrane disc.

The diametral compression test was performed on alumina discs. The samples used had a 27-mm diameter and were 3–4 mm thick, as shown in Fig. 5-8. An Instron universal testing machine was used to conduct the tests. The samples were diametrally pressed between flat plates with a crosshead speed of 0.01 mm/min. A fractured sample is shown in Fig. 5-9. It can be observed that the sample fractured into two halves, indicating that it underwent a tensile failure [58-60].

Fig. 5-9 shows the output of the diametral compression test showing the variation of compressive stress versus compressive strain. It was observed that the maximum compressive strength increased with the increase in silver content in the membrane of up to 20% of silver loading. This can be justified due to the improved dispersion of silver particles to hold together the CNTs. As a result, the mechanical strength of the membrane increased. The maximum strength of 8.5 MPa was observed for the sample with a 20% Ag content.

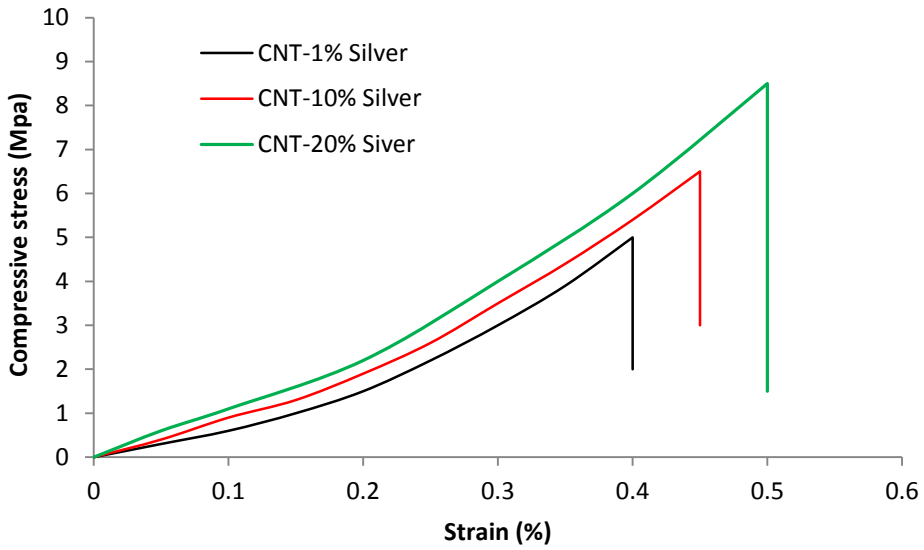


Figure 5-8: Diametral compression test curve

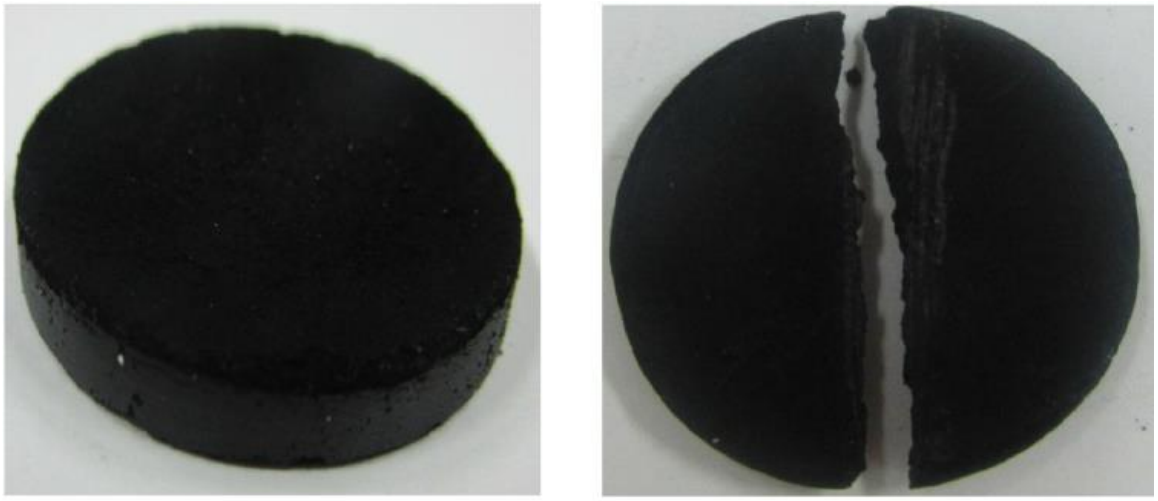


Figure 5-9: CNT-Ag membrane (a) Before diametral compression test (b) Fractured sample after being subjected to diametral compression test

5.7 Water Permeate Flux Measurement

Water transport through the membrane mainly depends on the hydrophilicity and porosity of the membrane. In general, the permeate flux is higher for hydrophilic membrane

surfaces with high porosity. Water permeate flux measurements were performed using a flow loop system, as shown in Fig. 5-10. A membrane with an effective area of 5.7 cm^2 that can be operated in the pressure range of 1 to 40 psi was used in the system. The flow loop system consisted of a membrane module, a feed tank with a 10-L capacity, two pressure gauges, flow meters and a high-pressure pump.

The pure water permeate flux was determined by Eq. (4):

$$J = \frac{V}{A.t} \qquad (4)$$

where J is the pure water permeate flux (L. m^{-2}. h^{-1}), V is the volume of permeate water measured in liters (L), and t is the time required for permeate water to pass through membrane (h).

The pure water permeate flux was measured under different conditions, as shown in Fig. 5-11 and 5-12. Initially, the water flux was measured at different transmembrane pressures, i.e., from 1 to 40 Psi. Then, the transmembrane pressure was maintained at 20 Psi for 30 min and the water permeate flux was measured. The same procedure was used to obtain the permeate flux for different pressures. Each pressure was maintained for 10 min before obtaining readings.

It can be seen from Fig. 5-11 that the permeate flux increases as the silver content increases. The higher permeate flux for membranes with higher silver loads can be justified on the basis of two mechanisms. First, at higher silver content, the membrane surface is more hydrophilic, as confirmed by the contact angle measurement. This leads to improved water transport through membrane. Second, due to the aggregation of silver

particles at higher loading, large pores are formed among the CNTs and silver particles; hence, the permeate flux will be higher. It can be seen that the two membranes CNT-10% Ag and CNT-20% exhibit permeate fluxes without application of any hydrostatic pressure difference. This indicated the hydrophilic nature of these membranes that enhance the permeated flux. However, the porosity is slightly lower when silver lead is 20% compared to that of 10% confirming therefore the less predominant character of the porosity compared to the hydrophobic character.

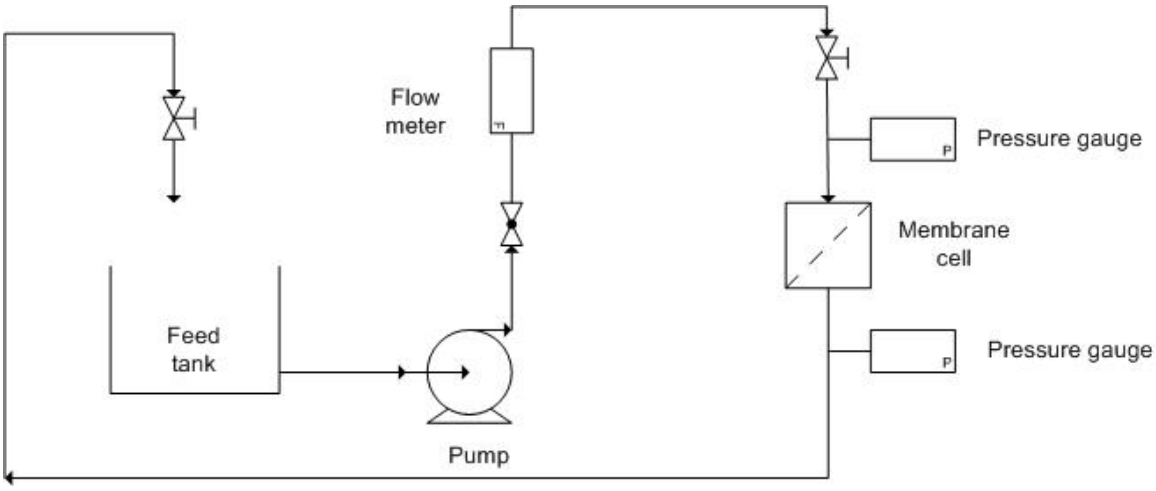


Figure 5-10: Schematic diagram of flow loop system

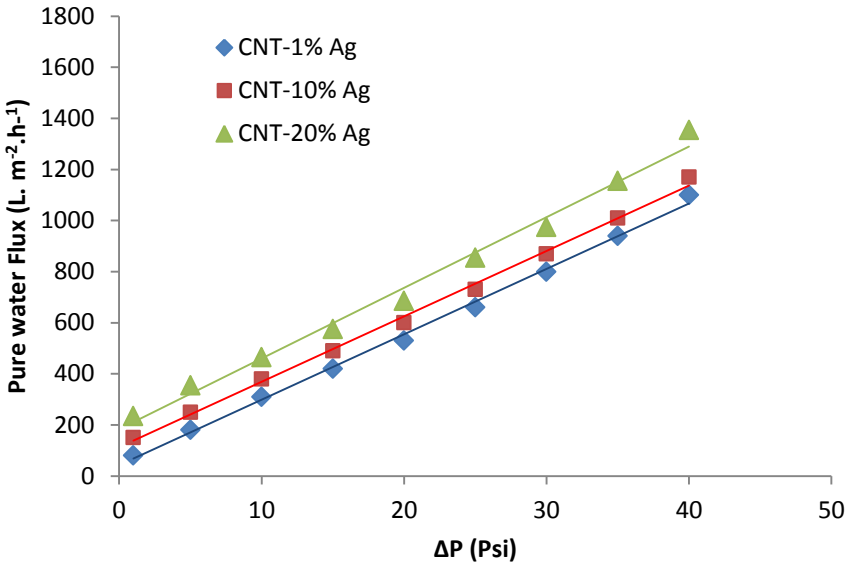


Figure 5-11: Effect of pressure and silver loading on pure water permeate flux

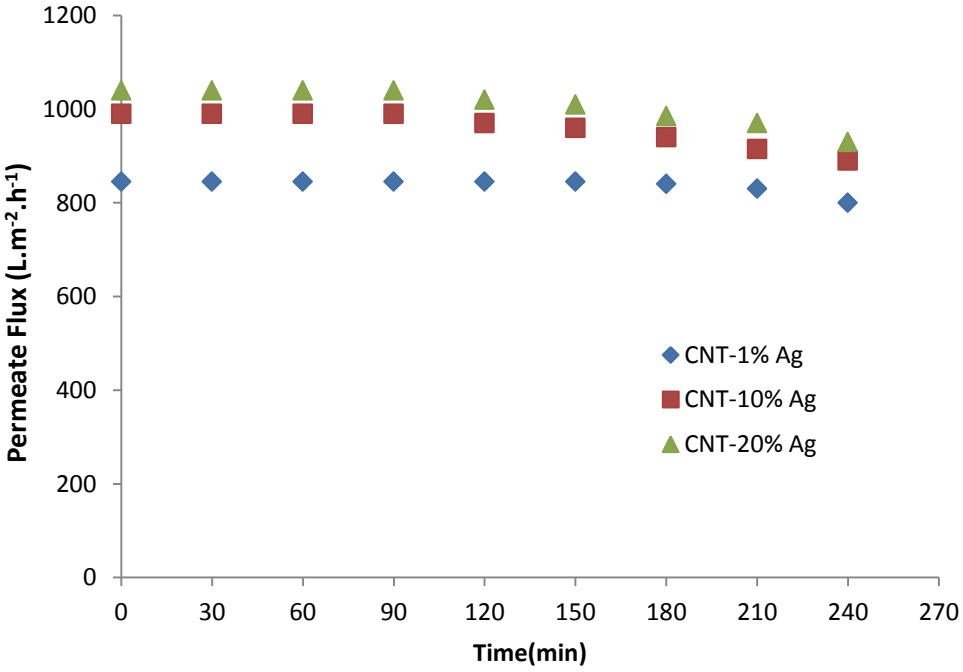


Figure 5-12: Effect of time on pure water permeate flux

5.8 Antibacterial Properties of the Membranes

The antibacterial properties of CNT-Ag membranes were evaluated using Escherichia coli (E. coli). In general, E. coli is selected as a model microorganism in photocatalytic experiments due to its wide use as a fecal contamination indicator. E. coli is a Gram-negative bacterium, and its cell membrane and cell wall have been described in detail [58-70].

Nutrient broth medium was prepared by dissolving 8 g of nutrient broth in 1000 ml of distilled water (pH adjusted to 7.5) and sterilizing at 121 ^{o}C at 2 bar pressure for 30 min. The wild-type *E. coli K12* (MG 1655) was grown overnight in nutrient broth at 37 ^{o}C on a rotary shaker (160 rpm). Aliquots of the broth medium containing E. coli were inoculated into fresh broth medium and incubated under the same conditions. Then, *E. coli* cells were harvested from the broth culture by centrifugation at 4000×g for 10 min at 4 ^{o}C, washing twice with a sterile 0.9% NaCl solution at 4 ^{o}C. The concentrated bacterial solution of E. coli was added to a 10-liter feed tank to have a starting bacterial concentration of 1×10^{6} colony forming units per milliliter (CFU/ml).

The test suspension of E. coli was filtered through the membranes with different loads of silver. The pressure was kept constant at 14.7 psi in all of the experiments. An agitator was used in the feed tank throughout during experiment to ensure the homogeneous mixing of the suspension. Samples (aliquots) were taken from the experimental setup at 0, 30, 60, 90, and 120 minutes. These aliquots were serially diluted with sterile normal saline, and aliquots from each dilution were inoculated separately on nutrient agar plates (in triplicate) and incubated at 37 ^{o}C. Colonies were counted after 48 h and compared with each other.

Fig. 5-13 shows the bacterial counts of the filtrate obtained after passing through the CNT membrane with different loads of silver. It can be observed that for the same initial concentration of bacterial suspension, the membrane with 10% silver content showed a tremendous antibacterial property. Almost 100% of bacterial were removed/killed by the CNT-10% Ag membrane after 1 hour. No bacterial cells were observed in the filtrates taken at 90 and 120 min for the membranes with 10 and 20% silver contents.

Fig. 5-14 to 5-16 shows the images of Luria-Bertani (LB) agar plates after an overnight culture of initial E. coli suspension and the filtrate obtained after passing the suspension across the membranes at different time intervals. These results confirmed that all of the membranes were effective in removing/killing the bacteria; however, the membrane with the 10% silver load showed the best anti-bacterial property.

With an increase in the silver loading from 10 to 20%, the time required to kill/remove the bacteria was increased. This might be due to the agglomeration of silver particles at 20% loading, which might produce large pores in the membrane. As a result, most of the bacterial will pass through the membrane. The maximum removal/killing by CNT membranes with 10% silver loads might be due to the good dispersion of silver in the matrix. Furthermore, the combined antitoxic properties of CNTs and silver led to enhanced antibacterial properties. These results are promising and confirmed the potential applications of these membranes in real water treatment systems. The possible mechanism involved might be the adsorption of E. coli on the silver doped CNTs surface at the initial stage and killing/removal by antitoxic properties of CNTs and silver. There is also possibility of bacteria removal by sieving once the pores are covered and blocked.

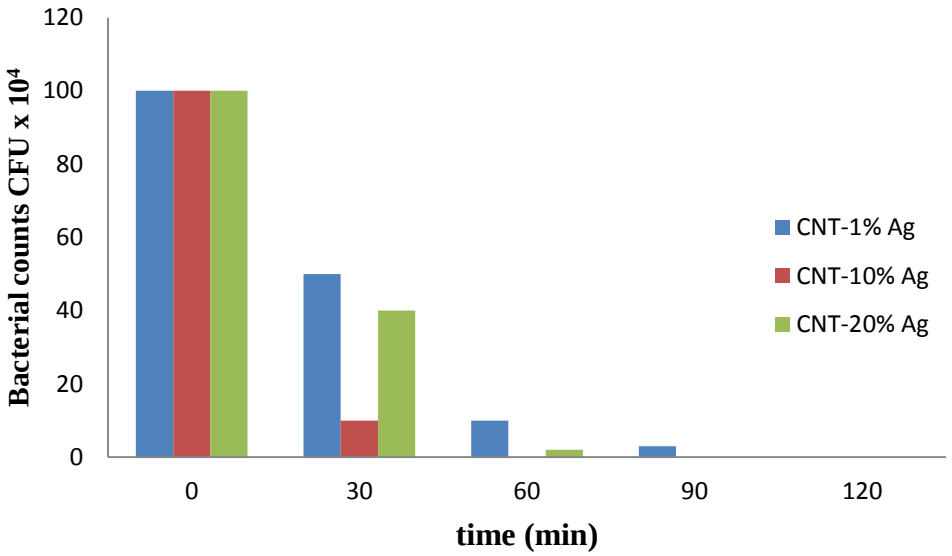


Figure 5-13: Bacterial counts CFU at various time intervals for CNT membrane with different loading of silver

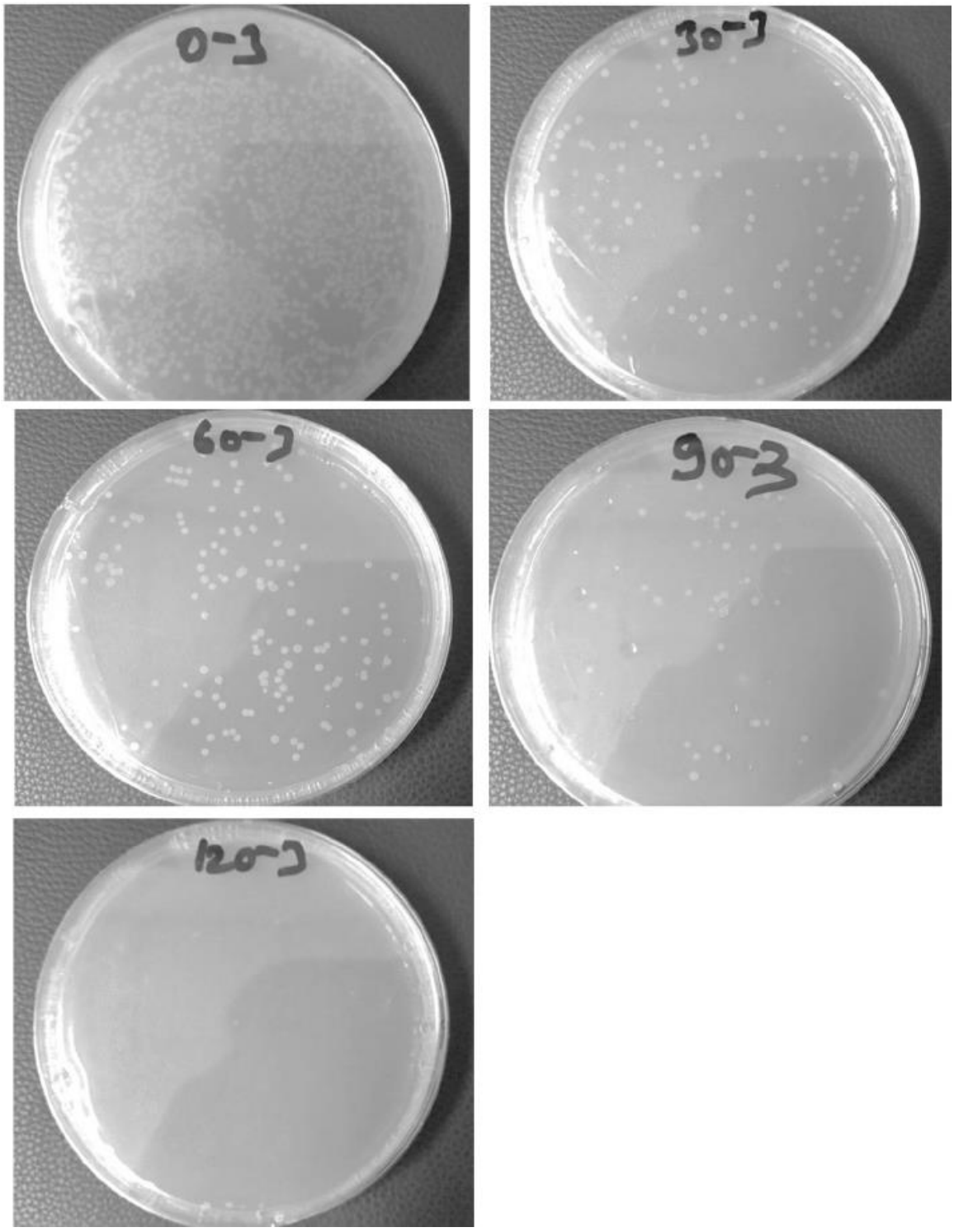


Figure 5-14: Images of Luria-Bertani (LB) agar plates after overnight culture of (a) Initial Ecoli suspension and the filtrate obtained after passing the suspension across 1% Ag-CNT membrane at (b) 30 (c) 60 (d) 90 (e) 120 min

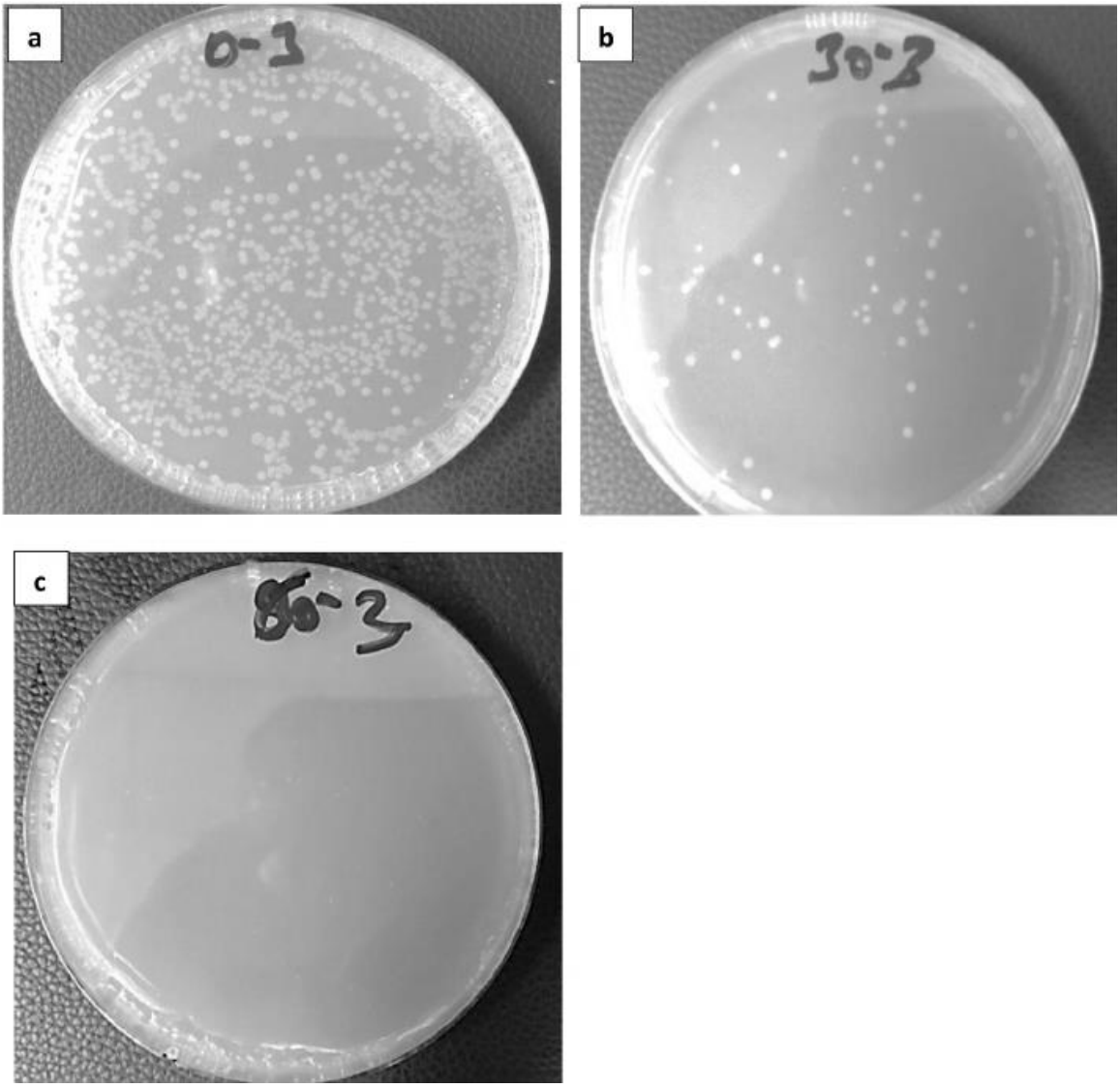


Figure 5-15: Images of Luria-Bertani (LB) agar plates after overnight culture of (a) initial Ecoli suspension and the filtrate obtained after passing the suspension across 10% Ag-CNT membrane at (b) 30 (c) 60 min

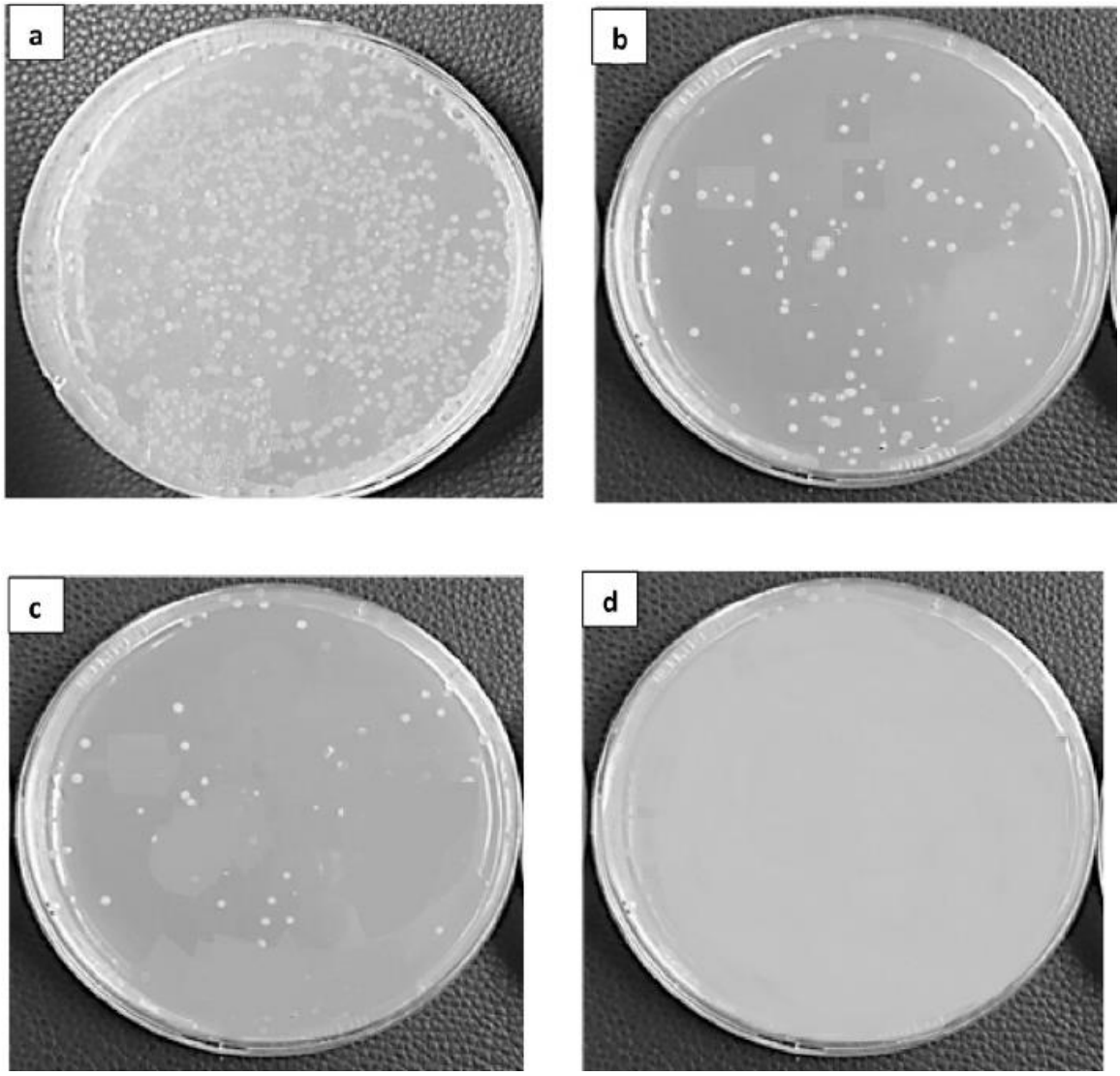


Figure 5-16: Images of Luria-Bertani (LB) agar plates after overnight culture of (a) initial Ecoli suspension and the filtrate obtained after passing the suspension across 20% Ag-CNT membrane at (b) 30 (c) 60 (d) 90 min

5.9 Conclusions

Silver-doped carbon nanotube membranes with a strong anti-bacterial potential were successfully synthesized using a novel approach. The membrane characteristics were remarkably influenced by the silver content. The silver not only affects the membrane properties but also serves as a welding agent to hold the CNTs together. As the loading of silver increased, it transformed the membrane from hydrophobic to hydrophilic, as confirmed by contact angle measurements. The porosity of the membrane was observed to increase with an increase in silver content from 1 to 10 %. All of the bacteria were removed/ killed by membranes with 10% silver loads after passing the suspension for 60 min only. The produced membrane has the potential to be employed in real water treatments system for the removal for a number of contaminants from wastewater.

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References

[1] X. Qu, P.J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res. 47 (2013) 3931–3946.

[2] S. Kar, R.C. Bindal, P.K. Tewari, Carbon nanotube membranes for desalination and water purification: Challenges and opportunities, Nano Today 7 (2012) 385-389.

[3] M. Cheryan. Ultrafiltration and Microfiltration Handbook. 2nd ed. CRC Press; 1998.

[4] C. Chen, J. Hu, D. Shao, J. Li, X. Wang, Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II), J. Hazard. Mater. 164 (2009) 923–928.

[5] Z. C.Di, Y.H. Li, Z.K. Laun, J. Liang, Adsorption of chromium(VI) ions from water by carbon nanotubes, Adsorpt. Sci. Technol. 22 (2004) 467–474.

[6] S.G.Wang, W.X. Gong, X.W. Liu, Y.W. Yao, B.Y. Gao, Q.Y. Yue, Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes, Sep. Purif. Technol. 58 (2007) 17–23.

[7] Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes, Carbon 4 (2003) 2787–2792.

[8] Ihsanullah**,** F. A. A. Khaldi, B. Abusharkh, M. Khaled, M.A. Atieh, M.S. Nasser, T. Laoui, S. Agarwal, I. Tyagi, V. K. Gupta, Adsorptive removal of Cadmium (II) ions from liquid phase using acid modified carbon-based adsorbents, J. Mol. Liq. 204 (2015) 255-263.

[9] Ihsanullah, F. A. A. Khaldi, B. A. Sharkh, A. M. Abulkibash, M. I. Qureshi, T. Laoui, M. A. Atieh, Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes, Desalin. water treat. (2015) doi: 10.1080/19443994.2015.1021847.

[10] C. Chen, X. Wang, Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes, Ind. Eng. Chem. Res. 45(2006) 9144–9149.

[11] L. Chen, K. Wang, M. Nagatsu, Europium adsorption on multiwall carbon nanotube/iron Oxide magnetic composite in the presence of polyacrylic acid, Environ. Sci. Technol. 43(2009) 2362–2367.

[12] B.Tawabini, S.A. Khaldi, M. Atieh, M. Khaled, Removal of mercury from water by multi-walled carbon nanotubes, Water Sci. Technol. 61(2010) 591-598.

[14] M. A. Atieh, O.Y. Bakather, B.S. Tawabini, A.A. Bukhari, M. Khaled, M. Alharthi, M.Fettouhi, F.A. Abuilaiwai, Removal of Chromium (III) from Water by Using Modified And Nonmodified Carbon Nanotubes. J. Nanomater. (2010) 232378.

[15] B.S. Tawabini, S.F. A. Khaldi, M. Khaled, M.A. Atieh, Removal of arsenic from water by Iron oxide nanoparticles impregnated on carbon nanotubes. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. 46(2011) 215–223.

[16] S. M. A. Hakami, A. B. Khalil, T. Laoui, M. A. Atieh, Fast Disinfection of Escherichia coli Bacteria Using Carbon Nanotubes Interaction with Microwave Radiation, Bioinorg. Chem. Appl. (2013) 458943.

[17] F. A. A. Khaldi, B. A. Sharkh, A. M. Abulkibash, M. A. Atieh, Cadmium Removal by Activated Carbon, Carbon Nanotubes, Carbon Nanofibers and Carbon Fly Ash: A Comparative Study, Desalin. Water Treat. 53 (2015) 1417-1429.

[18] A. Zeino, A. Abulkibash, M. Khaled, M. A. Atieh, Bromate Removal from Water using Doped Iron Nanoparticles on Multi-Walled Carbon Nanotubes (CNTs), J. Nanomater. (2014) 561920.

[19] C.H. Chen, C.C. Huang, Hydrogen adsorption in defective carbon nanotubes, Sep. Purif. Technol. 65 (2009) 305–310.

[20] A. Gaur, M. Shim, Substrate-enhanced O_2 adsorption and complexity in the Raman G-band spectra of individual metallic carbon nanotubes, Phys. Rev. B. 78 (2008) 1254221-1254227.

[21] K.M. Varlot, E. McRae, N.D. Pavlovsky, Comparative adsorption of simple molecules on carbon nanotubes dependence of the adsorption properties on the nanotube morphology, Appl. Surf. Sci. 196 (2002) 209–215.

[22] J. Goering, E. Kadossov, U. Burghaus, Adsorption kinetics of alcohols on single-wall carbon nanotubes: an ultrahigh vacuum surface chemistry study, J. Phys. Chem. C. 112 (2008) 10114–10124.

[23] H. Hyung, J.H. Kim, Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters, Environ. Sci. Technol. 42 (2008) 4416–4421.

[24] Ihsanullah, H.A. Asmaly, T.A. Saleh, T. Laoui, V.K. Gupta, M.A. Atieh, Enhanced adsorption of phenols from liquids by aluminum oxide/carbon

nanotubes: Comprehensive study from synthesis to surface properties, J. Mol. Liq. 206 (2015) 176-182.

[25] H. A. Asmaly, B. Abussaud, Ihsanullah, T. A. Saleh, V. K. Gupta, M. A. Atieh, Ferric Oxide Nanoparticles decorated Carbon nanotubes and carbon nanofibers: from synthesis to Enhanced Removal of Phenol, J. Saudi Chem. Soc. (2015). doi:10.1016/j.jscs.2015.06.002.

[26] S.Li, G. Liao, Z. Liu, Y. Pan, Q. Wu, Y. Weng, X. Zhang ,Z. Yang, O.K.C. Tsuid, Enhanced water flux in vertically aligned carbon nanotube arrays and polyethersulfone composite membranes, J. Mater. Chem. A. 2 (2014) 12171-12176.

[27] M. Majumder, N. Chopra, R. Andrews, B.J. Hinds, Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes, Nature 438 (2005) 44-44.

[28] J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes, Science 312 (2006) 1034-1037.

[29] P.S. Goh, A.F. Ismail , B.C. Ng, Carbon nanotubes for desalination: Performance evaluation and current hurdles, Desalination 308 (2013) 2–14.

[30] B.J. Hinds, N. Chopra, R. Andrews, V. Gavalas, L.G. Bachas, Aligned Multiwalled Carbon Nanotube Membranes, Science 303 (2004) 62-65.

[31] S.A. Miller, V.Y. Young, C.R. Martin, Electroosmotic Flow in Template-Prepared Carbon Nanotube Membranes, J. Am. Chem. Soc. 123 (2001) 12335-12342.

[32] W. Chengwei, L. Menke, P. Shanlin, L. Hulin, Well-aligned carbon nanotube array Membrane synthesized in porous alumina template by chemical vapor deposition, Chin. Sci. Bull. 45 (2000) 1373–1376.

[33] A. Srivastava, O.N. Srivastava, S. Talapatra, R. Vajtai, P.M. Ajayan, Carbon nanotube Filters, Nat. Mater. 3 (2004) 610–614.

[34] G.T. Pham, Y.B. Park, S. Wang, Z. Liang, B. Wang, C. Zhang, P. Funchess, L. Kramer, Mechanical and electrical properties of polycarbonate nanotube buckypaper composite Sheets, Nanotechnology 19 (2008) 325705.

[35] L.F. Dumee, K. Sears, J. Schütz, N. Finn, C. Huynh, S. Hawkins, M. Duke, S. Gray,Characterization and evaluation of carbon nanotube Bucky-Paper membranes for direct contact membrane distillation, J. Membr. Sci. 351 (2010) 36–43.

[36] S.M.Cooper, H.F. Chuang, M. Cinke, B.A. Cruden, M. Meyyappan, Gas permeability of a buckypaper Membrane, Nano Lett. 3 (2003) 189–192.

[37] R. Andrews, D. Jacques, A.M. Rao, F. Derbyshire, D. Qian, X. Fan, E.C. Dickey, J. Chen, Continuous production of aligned carbon nanotubes: A step closer to commercial realization, Chem. Phys. Lett. 303 (1999) 467–474.

[38] Y. Ma, F. Shi, Z. Wang, M. Wu, J. Ma, C. Gao, Preparation and characterization of PSf/clay nanocomposite membranes with PEG 400 as a pore forming additive, Desalination 286 (2012) 131–137.

[39] K. Ebert, D. Fritsch, J. Koll, C. Tjahjawiguna, Influence of inorganic fillers on the compaction behaviour of porous polymer based membranes, J. Membr. Sci. 233 (2004) 71–78.

[40] S. Majeed, D. Fierro, K. Buhr, J. Wind, B. Du, A.B.D. Fierro, V. Abetz, Multi-walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes, J. Membr. Sci. 403-404 (2012) 101– 109.

[41] D.L. Arockiasamy, J. Alam, M. Alhoshan, Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications, Appl. Water Sci. 3 (2013) 93–103.

[42] H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite, J. Membr. Sci. 362 (2010) 374–383.

[43] P. Shah, C.N. Murthy, Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal, J. Membr. Sci. 437 (2013) 90–98.

[44] J.B. Li, J.W. Zhu, M.S. Zheng, Morphologies and properties of poly(phthalazinone ether sulfone ketone) matrix ultrafiltration membranes with entrapped TiO_2 nanoparticles, J. Appl. Polym. Sci. 103 (2006) 3623–3629.

[45] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li,The influence of nano-sized TiO_2 fillers on the morphologies and properties of PSf UF membrane, J. Membr. Sci. 288 (2007) 231–238.

[46] X. Cao, J. Ma, X. Shi, Z. Ren, Effect of TiO_2 nanoparticle size on the performance of PVDF membrane, Appl. Surf. Sci. 253 (2006) 2003–2010.

[47] N.M. Wara, L.F. Francis, B.V. Velamakannim, Addition of alumina to cellulose acetate Membranes, J. Membr. Sci. 104 (1995) 43–49.

[48] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized Al_2O_3-particle addition on PVDF ultrafiltration membrane performance, J. Membr. Sci. 276 (2006) 162–167.

[49] A. Bottino, G. Capannelli, A. Comite, Preparation and characterization of novel porous PVDF-ZrO_2 composite membranes, Desalination 146 (2002) 35–40.

[50] P. Nunes, V. Peinemann, K. Ohlrogge, A. Alpers, M. Keller, N. Pires, Membranes of poly(ether imide) and nano dispersed silica, J. Membr. Sci. 157(1999) 219–226.

[51] Z. Xiu, Q. Zhang, H. L. Puppala,V. L. Colvin, P. J. J. Alvarez, Negligible Particle-Specific Antibacterial Activity of Silver Nanoparticles, Nano Lett. 12 (2012) 4271−4275.

[52] E.S. Kim, G. Hwang, M. G. E. Din, Y. Liu, Development of nanosilver and multi-walled carbon nanotubes thin-film nanocomposite membrane for enhanced water treatment, J. Membr. Sci. 394-395 (2012) 37–48.

[53] M. A. Ahmad, F.A.A. Aleem, A, Mutiri, Ubaisy, Biofuoling in RO membrane systems Part 1: Fundamentals and control, Desalination 132 (2000) 173-179.

[54] H.S. Vrouwenvelder, J.A.M.V. Paassen, H.C. Folmer, J.A.M.H. Hofman, M.M. Nederlof, D.V.D. KooiJ, Biofouling of membranes for drinking water production, Desalination 118 (1998) 157- 166

[55] H. Ridgway H, K. Ishida, G. Rodriguez, J. Safarik, T. Knoell, R. Bold, Biofouling of membranes: Membrane preparation, characterization, and analysis of bacterial adhesion, Methods. Enzymol.310 (1999) 463–494.

[56] N. Hilal, K. Victor, A. Laila, L. Tetyana, Surface modified polymeric membranes to reduce (bio)fouling: a microbiological study using E. coli, Desalination 15 (2004) 293–300.

[57] F. Liu, M. Abed, K. Li,Preparation and characterization of poly(vinylidene fluoride) PVDF) based ultrafiltration membranes using nano γ-Al_2O_3, J. Membr. Sci. 366 (2011) 97–103.

[58] R.J. Gohari, E. Halakoo, W. J. Lau, M. A. Kassim, T. Matsuura. A. F. Ismail. Novel polyethersulfone (PES)/hydrous manganese dioxide (HMO) mixed matrix membranes with improved anti-fouling properties for oily wastewater treatment process, RSC Adv. 4 (2014) 17587-17596.

[59] M. F. A. Goosen, S. S. Sablani, H. A. Hinai, S. A. Obeidani, R. A. Belushi. D. Jackson, Fouling of Reverse Osmosis and Ultrafiltration Membranes: A Critical Review, Sep. Sci. Technol. 39 (2005) 2261–2297.

[60] C. Huyskens, E. Brauns, E. V. Hoof, H. D. Wever, A new method for the evaluation of the reversible and irreversible fouling propensity of MBR mixed liquor, J. Membr. Sci. 323(2008) 185–192.

[61] D. Johnson, F. Galiano, S.A. Deowan, J. Hoinkis, A. Figoli, N. Hilal, Adhesion forces between humic acid functionalized colloidal probes and polymer membranes to assess fouling potential, J. Membr. Sci. 484 (2015) 35-46.

[62] N.F. Razali, A.W. Mohammad, N. Hilal, Effects of polyaniline nanoparticles in polyethersulfone ultrafiltration membranes: Fouling behaviors by different types of foulants foulants, J. Ind. Eng. Chem. 20(2014) 3134-3140 .

[63] I.N. H. M. Amin, A.W. Mohammad, N. Hilal, Description of membrane fouling characteristics during ultrafiltration of organic foulants contained in Sweetwater solutions. J. Environ. Chem. Eng. 2(2014) 1243-1251.

[64] S. Alzahrani, A.W. Mohammad, N. Hilal, P. Abdullah, O. Jaafar, Identification of foulants, fouling mechanisms and cleaning efficiency for NF and RO treatment of produced water, Sep. Purif. Technol. 118(2013) 324-341.

[65] M.N.A Seman, M. Khayet, N. Hilal, Comparison of two different UV-grafted nanofiltration membranes prepared for reduction of humic acid fouling using acrylic acid and N-vinylpyrrolidone, Desalination. 287(2012) 19-29.

[66] N. Hilal, O.O. Ogunbiyi, N.J. Miles, R. Nigmatullin, Methods employed for control of fouling in MF and UF membranes: A comprehensive review, Separ. Sci. Technol. 40(2005) 1957-2005.

[67] A. Alpatova, S. Verbych, M. Bryk, R. Nigmatullin, N. Hilal, Ultrafiltration of water containing natural organic matter: Heavy metal removing in the hybrid complexation ultrafiltration process, Sep. Purif. Technol. 40(2004) 155-162.

[68] N. Hilal, O. Ogunbiyi, J. Miles, Experimental investigation on the separation of bentonite using ceramic membranes: Effect of turbulence promoters, Separ. Sci. Technol. 43(2008) 286-309.

[69] W. Richard, N. Hilal, W. Lovitt, C.J. Wright, Characterisation of membrane surfaces:Direct measurement of biological adhesion using an atomic force microscope, J. Membr. Sci. 154 (1999) 205-212.

[70] W. R. Bowen, N. Hilal, R. W. Lovitt, C. J. Wright, Direct measurement of the force of adhesion of a single biological cell using an atomic force microscope, Colloids Surf. A Physicochem. Eng. Asp. 136(1998) 231-234.

CHAPTER 6

REMOVAL OF NOXIOUS HEXAVALENT CHROMIUM USING NOVEL CARBON NANOTUBE MEMBRANES

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Abstract

Metal oxide doped-carbon nanotubes were synthesized using a novel approach and employed for the removal of hexavalent chromium from aqueous solution. Aluminium oxide and iron oxide were impregnated on the surface of carbon nanotubes (CNTs). The loading of metal oxide was varied from 1 to 20 wt%. The impregnated CNTs were compacted at 300 MPa and sintered at 1400 ^{o}C to form a compact disc shape membrane. Experiments were performed in a continuous filtration system. The removal was affected by the metal oxide loading, initial solution concentration, pH and time. Maximum removal of 92% of Cr(VI) was observed by membrane with 10% Fe_2O_3 loading at pH 6 and initial concentration of 0.5 ppm after 3 hours of operation. Membrane with 10% Al_2O_3 was able to remove 79% of Cr(VI) ions under same experimental conditions. These results suggest that the metal oxide doped-carbon nanotube membrane can be effectively employed in continuous filtration system for the removal of Cr(VI) ions.

Keywords: *Membrane, metal oxide, water treatment, carbon nanotubes, hexavalent chromium.*

6.1 Introduction

Heavy metal ions are considered to be toxic to the environment due to their non-biodegradability and toxicity even at low concentrations [1, 2]. Among these, chromium is a well-known, highly toxic metal found in drinking water and is considered to be major pollutant. Chromium is found in natural deposits which contain other elements such as ferric chromite ($FeCr_2O_4$), chrome ochre (Cr_2O_3) and crocoite ($PbCrO_4$) [3, 4]. Industrial sources of chromium are wastewater from textile industry, wood preservation, glass industry, dyes and pigments, production of steel and alloys, mining of chrome ore, leather tanning, electroplating and metal cleaning [4-7].

Chromium is naturally found in different oxidation states including 2+, 3+ and 6+. It can exist in water as dichromate ($Cr_2O_7^{2-}$) ions, hydrogen chromate ion ($HCrO_4^-$), chromic acid (H_2CrO_4) and chromate ion (CrO_4^{2-}) [8-10]. However, the trivalent Cr(III) and hexavalent Cr(VI) are the most stable forms and most likely to be present in water in neutral pH range. Chromium concentration in industrial water varies from 5.2 to 208,000 mg/L [11-12]. The World Health Organization (WHO) has designated a guideline value of 0.05 mg/L for chromium in drinking water [13-16]. While the allowable limit for Cr (VI) in water as suggested by the US Environmental Protection Agency (EPA) is 0.1 mg/L [14-17].

This stringent limit of chromium in potable water by WHO is due to its severe toxicity to human body. However, Cr (VI) is more toxic (almost 300 times) than Cr(III) due to its mutagenic and carcinogenic nature [18]. Exposure to Cr(VI) may cause repository problems (asthma), internal hemorrhage, dermatitis, kidney and liver damage, dermatitis

and nausea. Skin and eye contact may cause nasal septum, ulceration, irritation, severe burn and permanent damage to eye [19-20].

Various techniques have been employed for the removal of Cr (VI) from water including membrane technologies [21-22], ion exchange [23-26], coagulation, flotation [27], solvent extraction [28], cyanide treatment [29] and adsorption [3,8-9].

However, most of these methods have limited applications due to economical or technical constraints. Water treatment by adsorption should provide the most economical and practical treatment alternative. Many adsorbents have been used to remove metal ions from wastewater, including biomaterials, zeolite, manganese oxides, kaolinite, resins, peanut hulls, algal biomass, recycled alum sludge and CNTs [1-2]. However, most of the adsorption techniques are batch level and unable to process large amount of contaminated water. Membrane process, on the other hand, separates the contaminants based on their size only and only specific membrane (nanofiltration range) can be employed to removal these pollutants.

The most common membrane processes used for treating wastewater containing heavy metals are ultra-filtration, nanofiltration and reverse osmosis [1-2]. A carbon based membrane has the advantage of heavy metal removal by adsorption in addition to sieving. Furthermore, the energy consumption is lower due to porous structure of the membrane.
CNTs have recently attracted considerable attention for synthesis of novel membranes with attractive features for water purification [30-31]. CNTs can also be used as direct filters and effective fillers to improve the membrane performance [32-33]. CNTs have proven to be excellent filler in membrane due to improved permeability, rejection,

disinfection and antifouling behavior. The flux of certain molecules through CNTs, as estimated by molecular dynamics (MD) simulation have been found to be 3-4 orders of magnitude higher than predicted by the Hagen-Poiseuille equation [32-34].

This paper describes the application of metal oxide impregnated carbon nanotube membranes for the removal of Cr(VI). The loading of metal oxide was varied from 1 to 20 wt%. The experiments were performed in a continuous flow loop system. The effect of pH, metal oxide loading in the membrane, initial concertation of the solution and time weas investigated on the removal of Cr(VI).

6.2 Experimental Details

6.2.1 Membrane Preparation and Characterizations

Carbon nanotubes impregnated with Fe_2O_3 and Al_2O_3 nanoparticles were synthesized and characterized using the procedure described in the previous chapters. The impregnated CNTs were characterized by Scanning Electron Microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD) and Thermogravimetric Analysis (TGA), while the membranes were characterized by measuring their porosity, contact angle, diametrical compression test and pure water flux [30-31].

6.2.2 Water Flux Measurement

Water flux measurements were performed using a flow loop system, as shown in Fig. 6-1. The flow loop system consisted of a membrane module, a feed tank with 10 L capacity, two pressure gauges, flow meters and a high-pressure pump.

The pure water flux was determined by Eq. (1):

$$J = V/A.t \qquad (1)$$

where J is pure water flux ($L.m^{-2}.h^{-1}$), V is the volume of permeate water measured in liter (L), and t the time in hours required for permeate water to pass through membrane (h). The optimum pressure of 14.7 psi was used in all heavy metal removal experiments.

The pure water permeate flux was measured under different conditions, as shown in Fig. 6-2. Initially, the water flux was measured at different transmembrane pressures, i.e., from 1 to 40 psi. Then, the transmembrane pressure was maintained at 20 psi for 30 min and the water permeate flux was measured. The same procedure was used to obtain the permeate flux for different pressures. Each pressure was maintained for 10 min before recording readings. It can be seen from Fig. 6-2 that the permeate flux increases as the metal oxide content increases. The higher permeate flux for membranes with higher metal oxide loads can be justified on the basis of two mechanisms. First, at higher metal oxide content, the membrane surface is more hydrophilic, as confirmed by the contact angle measurement [30-31]. This leads to improved water transport through membrane. Second, due to the aggregation of metal oxide particles at higher loading, large pores are formed among the CNTs; hence, the permeate flux is higher.

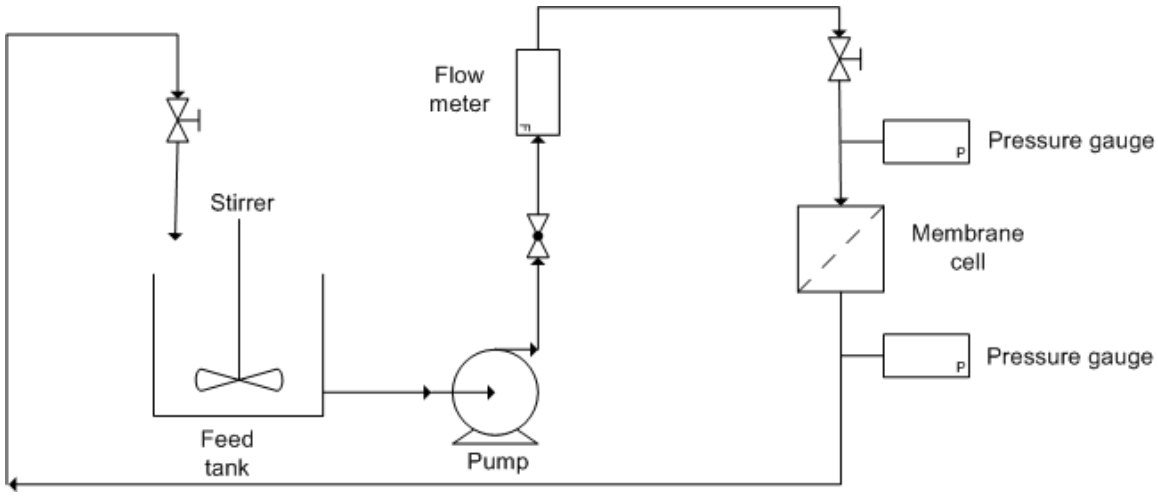
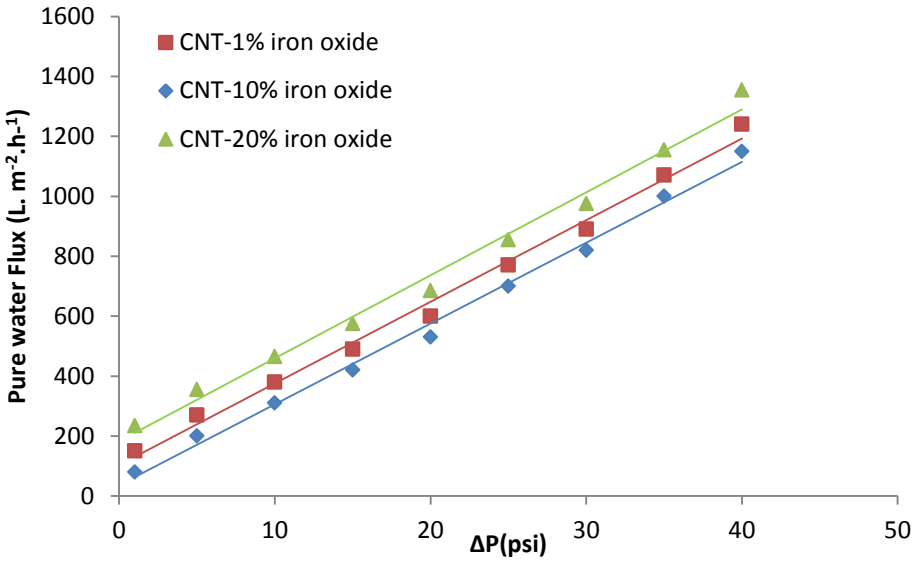
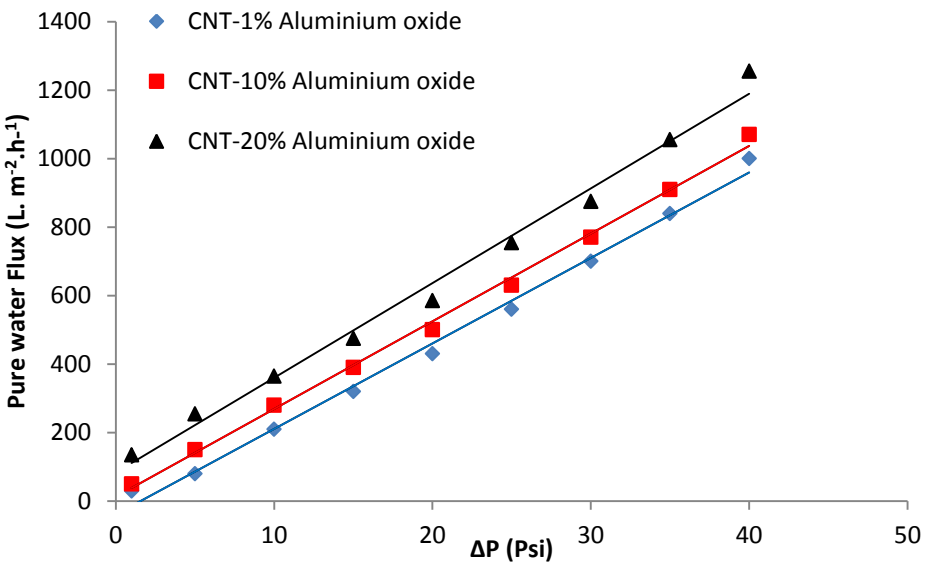


Figure 6-1: Schematic diagram of flow loop system



(a)



(b)

Figure 6-2: Effect of transmembrane pressure on pure water flux on (a) CNT-Fe_2O_3 (b) CNT-Al_2O_3 membrane

6.2.3 Hexavalent Chromium Removal

Hexavalent chromium solution of 1 ppm with an initial volume of approximately 10 L was prepared in the feed tank. The solution pH was adjusted using 1M NaOH or 1M HNO_3. The pressure and flow rate were adjusted accordingly and the solution is pumped continuously through the membrane. Permeate was collected at different time intervals. The effect of initial concentration, time and loading of metal oxide in membrane was studied on the removal of Cr(VI). Inductively coupled plasma mass spectrometry (ICP-MS) was employed to measure the concentration of Cr(VI) before and after the flux experiment.

The removal can be determined using the equation:

$$R = 1 - C_p/C_f \qquad (2)$$

where C_p and C_f are the concentrations of solute in permeate and feed, respectively.

Table 6-1 shows the experimental conditions for the removal of Cr(VI) using different CNT-Fe_2O_3 and CNT-Al_2O_3 membranes.

Table 6-1: Experimental conditions

Exp No.	Membrane	Pressure (psi)	pH	Concentration (ppm)
1	CNT-10% Fe_2O_3	14.7	3,6,8	1
2	CNT-1% Fe_2O_3	14.7	6	1,5,10
3	CNT-10% Fe_2O_3	14.7	6	1,5,10
4	CNT-20% Fe_2O_3	14.7	6	1,5,10
5	CNT- 10%Al_2O_3	14.7	3,6,8	1
6	CNT- 1%Al_2O_3	14.7	6	1,5,10
7	CNT- 10%Al_2O_3	14.7	6	1,5,10
8	CNT- 20%Al_2O_3	14.7	6	1,5,10

6.3 Results and Discussion

6.3.1 Effect of Feed pH

Solution pH is an important parameter to determine the removal of heavy metal by carbon based materials. The Cr(VI) removal experiments were performed using the membranes with 10% aluminium oxide and iron oxide loading in the pH range 3-8. Results of the analysis are shown in Fig. 6-3.

The effect of pH on adsorption of Cr(VI) ions can be explained on the basis of ionic chemistry of the solution and surface charge of the adsorbents. Depending upon the

chromate concentration and solution pH, Cr(VI) may exists in different ionic states including hydrogen chromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$) and chromate (CrO_4^{2-}). The equilibrium between the chromate (CrO_4^{2-}) and dichromate ions ($Cr_2O_7^{2-}$) in aqueous solution is shown by the reaction (equation 3) [17, 35].

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O \qquad (3)$$

Dichromate ions ($Cr_2O_7^{2-}$) are the dominant species at low pH, while at high pH, only chromate (CrO_4^{2-}) ions exists in the solution. At low pH, the dominant species $Cr_2O_7^{2-}$ is converted to $HCrO_4^-$, which can be easily turned to Cr(III) ions due to high redox potential (1.33V), as shown by equations 4 & 5 [29,37].

$$Cr_2O_7^{2-} + H_2O \quad \leftrightarrow \quad 2HCrO_4^- \qquad (4)$$

$$HCrO_4^- + 7H^+ + 3e \rightarrow Cr(III) + H_2O \qquad E_o = 1.33V \qquad `(5)$$

However, at high pH, the dominant species chromate (CrO_4^{2-}) is converted to a precipitate of $Cr(OH)_3$ due to low redox potential (-0.13V), as shown in equation (6) [17,36]

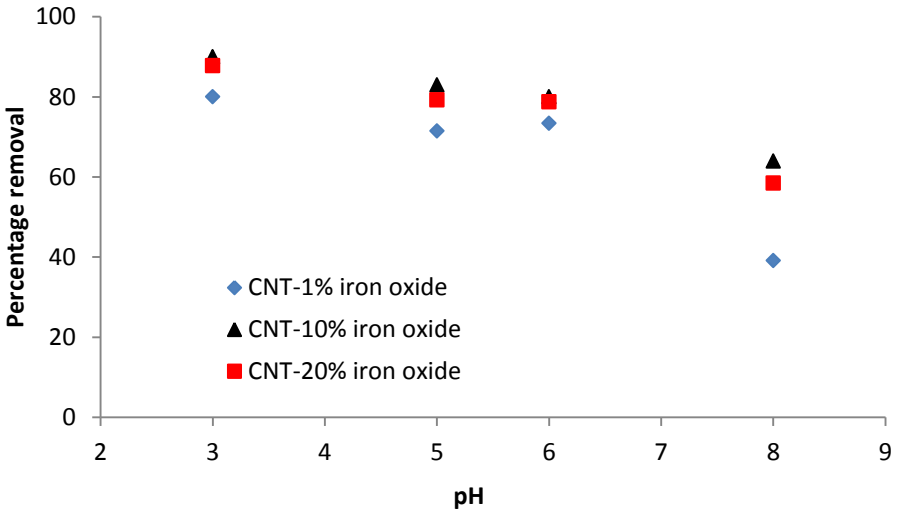
$$Cr_2O_7^{2-} + H_2O + 3e \rightarrow Cr(III) + 5OH^- \qquad E_o = -0.13V \qquad (6)$$

From Fig. 6-3, it can be seen that the removal efficiency of Cr(VI) for all the membranes is higher at low pH values. This can be explained on the basis of the positively charged surface of the membranes at lower pH. The electrostatic interaction between the positively charged adsorbents surface and $Cr_2O_7^{2-}$ anions is responsible for higher removal efficiency of Cr(VI) at low pH. However, at high pH, the Cr(VI) removal efficiency is lower due to competition between the chromate (CrO_4^{2-}) and OH^- ions, to

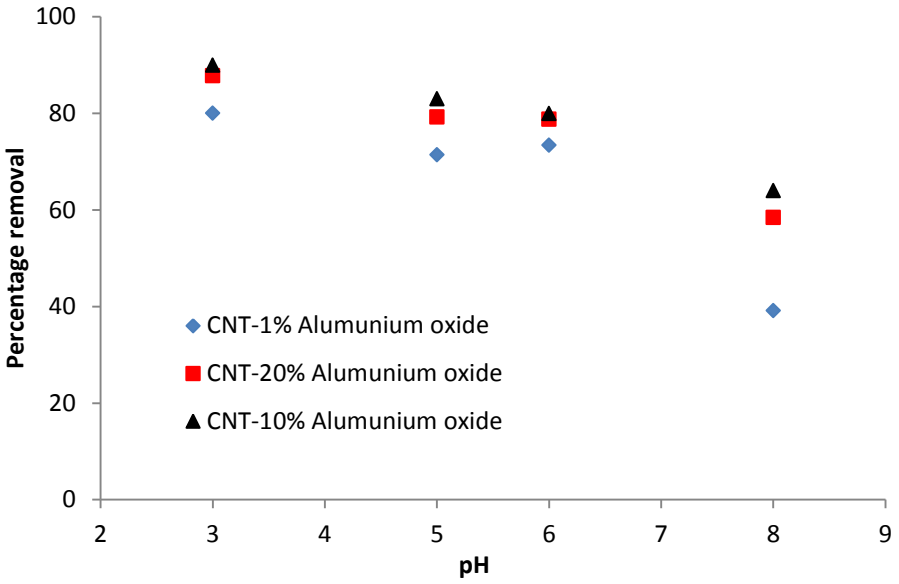
cover the limited adsorption sites. Furthermore, surfaces of the adsorbents carry more negative charges, which lead to repulsion between the adsorbents surface and CrO_4^{2-} ions.

As shown in Fig. 6-4, the point of zero electric charge (pH_{PZC}) value for aluminium oxide and iron oxide doped CNTs are 7 and 6.2, respectively. This demonstrated that both metal oxides show a basic character [38]. At pH < pH_{PZC}, the membrane surface is positively charged and attraction exists between the surface and Cr(VI) ions yielding high removal. At pH > pH_{PZC}, the surface of the membrane becomes more negatively charged and repulsion between Cr (VI) ions and negative surface is responsible for the low removal.

Although the maximum removal was observed at pH 3, however, the membranes also showed significant removal of Cr (VI) at pH 6. As the typical pH of drinking water is in the range of 6-8, therefore, all the experiments were performed at pH 6 to explore the potential of these membranes for Cr(VI) removal for practical applications.



(a)



(b)

Figure 6-3: Effect of pH on the percentage removal of hexavalent chromium ions by (a) CNT- Fe_2O_3 and (b) CNT-Al_2O_3 membrane (initial concertation=1ppm, time=3 hours)

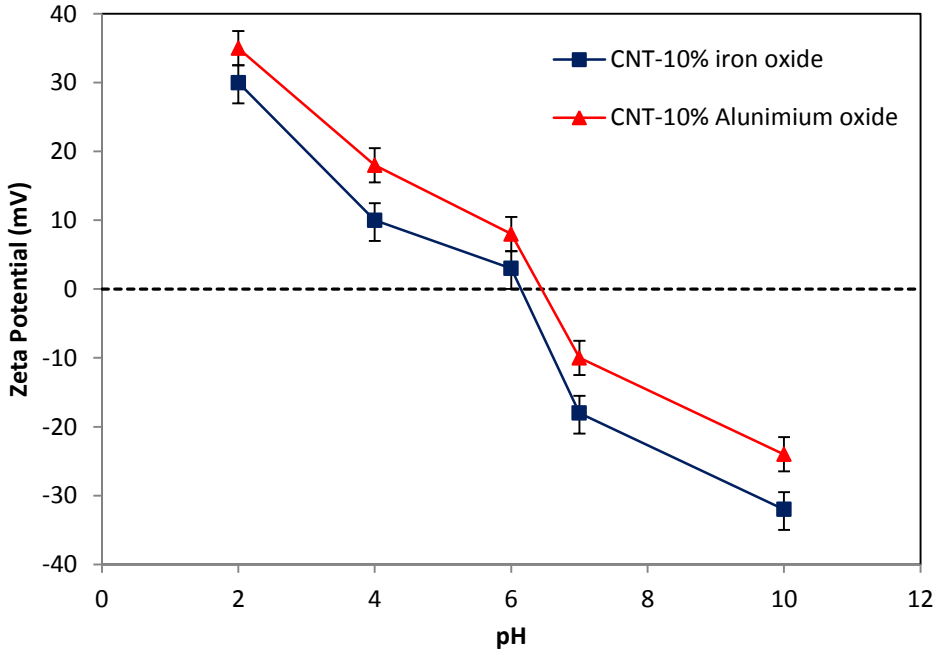


Figure 6-4: Variation of zeta potential values with pH of CNT-Al_2O_3 and CNT-Fe_2O_3

6.3.2 Effect of Initial Concentration

Fig. 6-5 presents the effect of initial concentration of the solution on the percentage removal of Cr(VI) ions. Initial concentration of the solution was varied from 0.5 to 10 ppm, while the other experimental conditions were pH 6, time 3 hours and transmembrane pressure 14.7 psi. It can be deduced that a maximum removal of 92 and 79 % is achieved by CNT-Fe_2O_3 and CNT-Al_2O_3, respectively at 0.5 ppm. The removal decreases with increase in initial concentration from 0.5 to 10 ppm. This might be due to the fact that at high concentration, all the available adsorption sites are expected to be covered by the Cr(VI) ions.

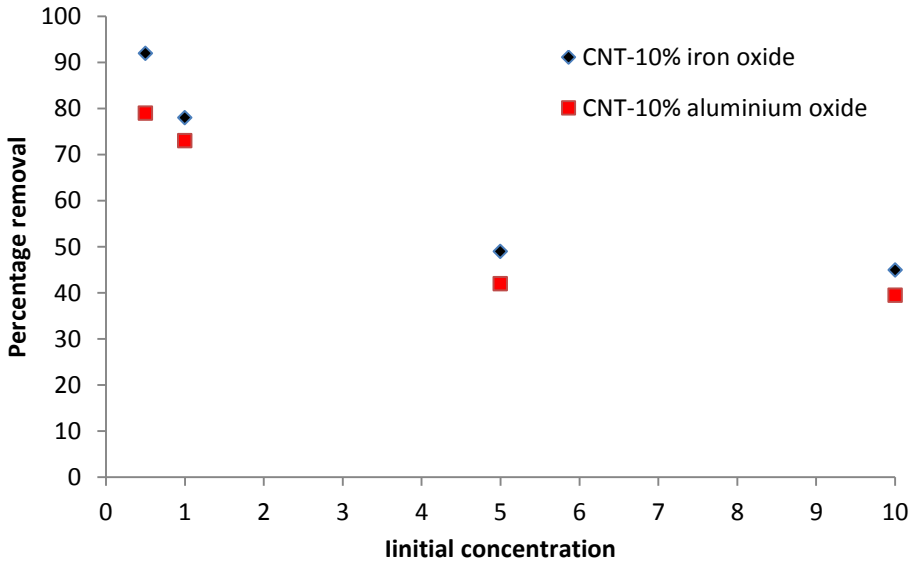


Figure 6-5: Effect of initial concertation on the percentage removal of Cr(VI) ions by CNT- 10% Fe_2O_3 and CNT-10% Al_2O_3 membranes (contact time=3 hours, pH 6)

6.3.3 Effect of Time

In order to study the effect of time on the removal of Cr(VI) ions, the experiments were performed under constant pH 6 and initial concentration of 0.5 ppm. The samples were

collected after every 30 min and analyzed. Results of the analysis are presented in Fig. 6-6. It can be seen that the percentage removal of Cr(VI) increases with increase in time until 3 hours of operation. After 3 hours, no significant increase in removal is observed and the equilibrium is achieved for all the membranes. Maximum removal of 92% is achieved with CNT-10% Fe_2O_3 membrane in 3 hours. The higher removal at 10% iron oxide loading might be due to uniform distribution and attachment of the Fe_2O_3 particles to the CNTs surface. At 1% loading, the Fe_2O_3 particles might not cover the spaces between the CNTs properly and few adsorption sites are introduced. At higher loading of 20%, some agglomeration takes place leading to increase in porosity. Due to higher porosity, the water flux is high and the contact time between the metal ions and membrane surface is reduced.

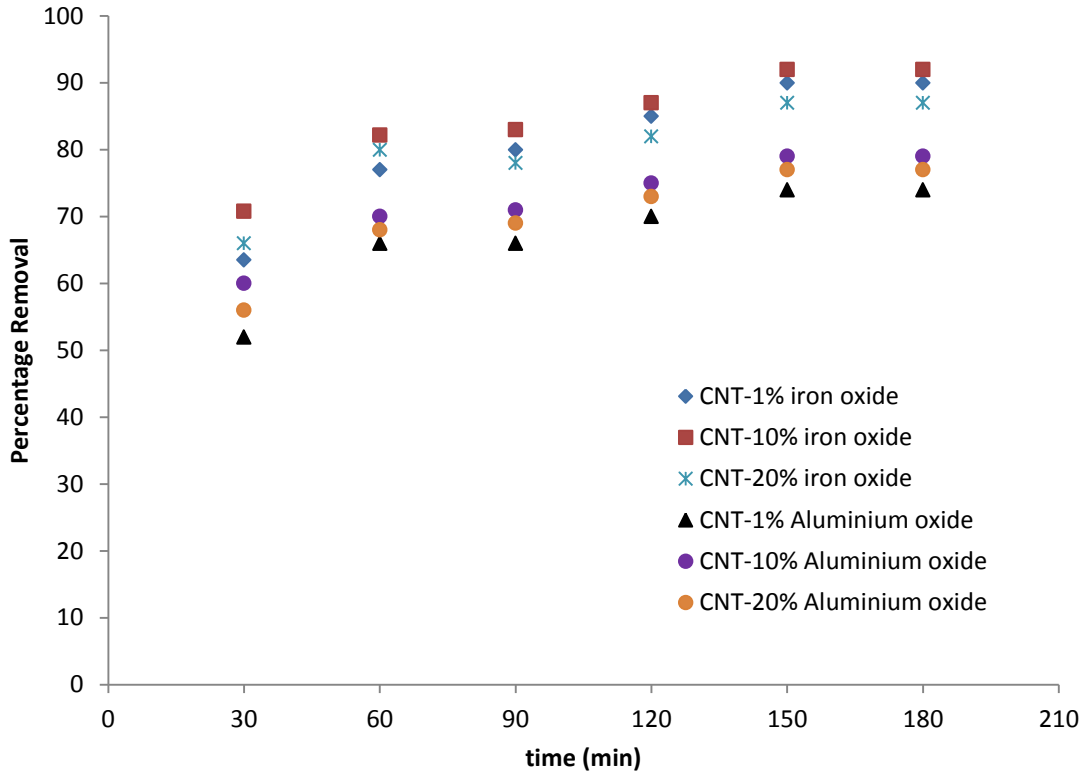


Figure 6-6: Effect of time on the percentage removal of hexavalent chromium ions by CNT- Fe_2O_3 and CNT- Al_2O_3 membranes (initial concertation=0.5 ppm, pH 6)

6.4 Conclusions

Metal oxide-doped carbon nanotube membranes were successfully synthesized using a novel approach. The membrane was able to remove low concentration of Cr(VI) ions from aqueous solution in a continuous flow loop system. The removal was affected by the metal oxide loading, initial solution concentration, pH and time. Maximum removal of 92% of Cr(VI) was observed at pH 6 and initial concentration of 0.5 ppm by CNTs membrane with 10% Fe_2O_3 loading after 3 hours of operation. Membrane with 10% Al_2O_3 was able to remove 79% of Cr(VI) ions under similar experimental conditions. These results suggest that the CNT- metal oxide membrane can be effectively employed in continuous filtration system for the removal of Cr(VI) ions.

References

[1] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arabian J. Chem. 4 (2011) 361–377.

[2] F. Fu, Q.Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407-418.

[3] D. Mohan, C.U. Pittman Jr., Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2006) 762–811.

[4] B.M. Weckhuysen, I.E. Wachs, R.A. Schoonheydt, Surface chemistry and spectroscopy of chromium in inorganic oxides, Chem. Rev. 96(8) (1996) 3327–3350.

[5] S. Kalidhasan, M. Ganesh, S. Sricharan, N. Rajesh, Extractive separation and determination of chromium in tannery effluents and electroplating waste water using tribenzylamine as the extractant, J. Hazard. Mater. 165 (2009) 886–892.

[6] J.R. Rao, P. Thanikaivelan, K.J. Sreeram, B.U. Nair, Green route for the utilization of chrome shavings (chromium-containing solid waste) in tanning industry, Environ. Sci. Technol. 36 (2002) 1372–1376.

[7] S. Vasudevan, G. Sozhan, S.Mohan, R. Balaji, P. Malathy, S. Pushpavanam, Electrochemical regeneration of chromium containing solution from metal finishing industry, Ind. Eng. Chem. Res. 46 (2007) 2898–2901.

[8] A.K. Bhattachaya, T.K. Naiya, S.N. Mandal, S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J. 137 (2008) 529–541.

[9] D. Mohan, K.P. Singh, V.K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Ind. Eng. Chem. Res. 44 (2005) 1027–1042.

[10] D. Mohan, K.P. Singh, V.K. Singh, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, J. Hazard. Mater. 135 (2006) 280–295.

[11] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review, J. Hazard. Mater. 180 (2010) 1–19.

[12] F.C. Richard, A.C.M. Bourg, Aqueous geochemistry of chromium: A review, Water Res. 25 (1991) 807–816.

[13] J. Zhu, H. Gu, J. Guo, M. Chen, H. Wei, Z. Luo, H.A. Colorado, N. Yerra, D. Ding, T.C. Ho, N. Haldolaarachchige, J. Hopper, D.P. Young, Z. Guo, S. Wei, Mesoporous magnetic carbon nanocomposite fabrics for highly efficient Cr(VI) removal, J. Mater. Chem. A 2 (2014) 2256–2265.

[14] B. Qiu, C. Xu, D. Sun, H. Wei, X. Zhang, J. Guo, Q. Wang, D. Rutman, Z. Guo, S. Wei, Polyaniline coating on carbon fiber fabrics for improved hexavalent chromium removal, RSC Adv. 4 (2014) 29855–29865.

[15] B. Qiu, C. Xu, D. Sun, H. Yi, J. Guo, X. Zhang, H. Qu, M. Guerrero, X. Wang, N. Noel, Z. Luo, Z. Guo, S. Wei, Polyaniline coated ethyl cellulose with improved hexavalent chromium removal, ACS Sustainable Chem. Eng. 2 (2014) 2070–2080.

[16] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium (VI) adsorption from aqueous solution by sawdust activated carbon, J. Hazard. Mater. 124 (2005) 192–199.

[17] C. Xu, B. Qiu, H. Gu, X. Yang, H. Wei, X. Huang, Y. Wang, D. Rutman, D. Cao, S. Bhana, Z. Guo, S. Wei, Synergistic interactions between activated carbon fabrics and toxic hexavalent chromium, ECS J. Solid State Sci. Technol. 3(3) (2014) M1–M9.

[18] K.K. Krishnani, S. Ayyappan, Heavy metals remediation of water using plants and lignocellulosic agrowastes, Rev. Environ. Contam. Toxicol. 188 (2006) 59–84.

[19] M. Aliabadi, I. Khazaei, H. Fakhraee, M.T.H. Mousavian, Hexavalent chromium removal from aqueous solutions by using low-cost biological wastes: Equilibrium and kinetic studies, Int. J. Environ. Sci. Technol. 9 (2012) 319–326.

[20] D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman, C.A. Mabuni, A. Critical, A critical assessment of chromium in the environment, Crit. Rev. Environ. Sci. Technol. 29 (1999) 1–46.

[21] C.A. Kozlowski, W. Walkowiak, Removal of chromium(VI) from aqueous solutions by polymer inclusion membranes, Water Res. 36 (2002) 4870–4876.

[22] H.F. Shaalan, M.H. Sorour, S.R. Tewfik, Simulation and optimization of a membrane system for chromium recovery from tanning waste, Desalination 141 (2011) 315–324.

[23] G. Tiravanti, D. Petruzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, Water Sci. Technol. 36 (1997) 197–207.

[24] S. Rengaraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater. 87 (2001) 273–287.

[23] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H, J. Hazard. Mater. 102 (2003) 257–275.

[25] D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, Ind. Eng. Chem. Res. 34 (1995) 2612–2617.

[27] K.A. Matis, P. Mavros, Recovery of metals by ion flotation from dilute aqueous solutions, Sep. Purif. Meth. 20 (1991) 1–48.

[28] E. Salazar, M.I. Ortiz, A.M. Urtiaga, J.A. Irabien, Equilibrium and kinetics of chromium(VI) extraction with Aliquat 336, Ind. Eng. Chem. Res. 31 (1992) 1516–1522.

[29] L. Monser, N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, Sep. Purif. Technol. 26 (2002) 137–146.

[30] Ihsanullah, T. Laoui, A.M. Al-Amer, A. B. Khalil, A. Abbas, M. Khraisheh, M. A. Atieh, Novel anti-microbial membrane for desalination pretreatment: A silver nanoparticle-doped carbon nanotube membrane, Desalination 376 (2015) 82-93.

[31] Ihsanullah, A.M. Al-Amer, A. Abbas, T. Laoui, N. Al-Aqeeli, F. Patel, M. Khraisheh, M. A. Atieh, N. Hilal, Fabrication and antifouling behaviour of a carbon nanotube membrane, Mater. Design 89 (2016) 549-558.

[32] J.K. Holt, A. Noy, T. Huser, D. Eaglesham, O. Bakajin, Fabrication of a carbon Nanotube-cmbedded silicon nitride membrane for studies of nanometer-scale mass transport, Nano Lett. 4 (2004) 2245-2250.

[33] S.Li, G. Liao, Z. Liu, Y. Pan, Q. Wu, Y. Weng, X. Zhang ,Z. Yang, O.K.C. Tsuid, Enhanced water flux in vertically aligned carbon nanotube arrays and polyethersulfone composite membranes, J Mater Chem A. 2 (2014) 12171-12176.

[34] M. Majumder, N. Chopra, R. Andrews, B.J. Hinds, Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes, Nature 438 (2005) 44-44.

[35] H. Gu, S.B. Rapole, Y. Huang, D. Cao, Z. Luo, S. Wei, Z. Guo, Synergistic interactions between multi-walled carbon nanotubes and toxic hexavalent chromium, J. Mater. Chem. A 1 (2013) 2011–2021.

[36] J. Zhu, S. Wei, H. Gu, S.B. Rapole, Q. Wang, Z. Luo, N. Haldolaarachchige, D.P. Young, Z. Guo, One-pot synthesis of magnetic graphene nanocomposites

decorated with core@double-shell nanoparticles for fast chromium removal, Environ. Sci. Technol. 46 (2012) 977–985.

[37] C.J. Lin, S.L. Wang, P.M. Huang, Y.M. Tzou, J.C. Liu, C.C. Chen, J.H. Chen, C. Lin, Chromate reduction by zero-valent Al metal as catalyzed by polyoxometalate, Water Res. 43(20) (2009) 5015–5022.

[38] J. Liang, J. Liu, X. Yuan, H. Dong, G. Zeng, H. Wu, H. Wang, J. Liu, S. Hua, S. Zhang, Z. Yu, X. He, Y. He, Facile synthesis of alumina-decorated multi-walled carbon nanotubes for simultaneous adsorption of cadmium ion and trichloroethylene, Chemical Engineering Journal 273 (2015) 101–110

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Metal oxide-doped carbon nanotube membranes were successfully synthesized using a novel approach. Iron oxide, aluminum oxide and silver nanoparticles were impregnated on the surface of CNTs. Metal oxide particles not only affected the membrane properties but also served as a welding agent to bond the CNTs together.

The permeate flux and rejection rate of sodium alginate (SA) were determined to predict the antifouling behavior of the iron oxide-doped carbon nanotube membranes. All the iron oxide doped CNT membranes were effective in removing the SA from water. A maximum removal of 90 and 88% of SA was achieved for membranes with a 10 and 1 wt% iron oxide content, respectively, after 3 h. A maximum flux of 1490 $L \cdot m^{-2} \cdot h^{-1}$ was observed for the membrane with a 50 wt% iron oxide content. The presence of iron oxide particles transformed the CNT-based membrane from hydrophobic to hydrophilic, as confirmed by contact angle measurement. A maximum tensile strength of 11.2 MPa was observed for the membrane containing 20% iron oxide. A negligible reduction in the permeate flux was observed with time for all membranes.

The silver-doped CNT membranes showed a high water permeate flux and exhibited strong antibacterial properties. The affinity of the membranes to biofouling was studied using Escherichia coli (E. coli) bacteria. All of the membranes with different silver loadings were able to remove/kill 100% of the bacteria; however, the CNT membrane

with 10 wt% silver showed a superior performance to the other membranes with 1 and 20 wt% silver loading. All bacteria were removed/killed in only 60 min by the membrane with 10 wt% silver loading after the suspension was passed through the membrane. The combined antitoxic properties of silver and CNTs led to enhanced antibacterial properties.

Metal-oxide doped-carbon nanotube membranes were also employed for the removal of hexavalent chromium from aqueous solution. Experiments were performed in a continuous filtration system. The removal was affected by the metal oxide loading, initial solution concentration, pH and time. Maximum removal of 92% of Cr(VI) was observed at pH 6 and initial concentration of 0.5 ppm by membrane with 10% Fe_2O_3 loading after 3 h of operation. Membrane with 10% Al_2O_3 was able to remove 79% of Cr(VI) ions under similar experimental conditions. These results suggest that the CNT- metal oxide membrane can be effectively employed in continuous filtration system for the removal of Cr(VI) ions. These membranes would be advantageous in a continuous filtration system for the removal of different contaminants from water via desalination, adsorption and sieving.

7.2 Recommendations

Based on the current work, some recommendations are made for the successful implementation of the CNTs membranes in water treatment.

- The major challenge in the synthesis of carbon nanotube membranes is the comparative low mechanical strength. It is recommended to explore other materials to be used as welding agent for holding the CNTs together with the aim to enhance the mechanical strength of the membranes.
- Furthermore, work should be done to control the porosity of the membrane.
- It is recommended to use the CNTs with open tips so that the inner channels can also be used as a flow path for water molecules.
- The orientation of CNTs can also affect the flux and removal of contaminants. It is suggested to explore the techniques for the alignment of CNTs for the improved performance.
- The CNT membranes might have potential application in desalination. The use of CNT membranes as an electrode might be a breakthrough in this field.
- Besides CNTs, the potential of other members of carbon family should be explored for the synthesis of similar membranes.
- One of the major challenges for the practical implantation of CNT membrane is the cost of CNTs. Development of novel techniques for the large scale production of CNTs with a cost effective procedure will be helpful for the practical application of these membranes in commercial water treatment plants.

Curriculum Vitae

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PERSONAL INFORMATION

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EDUCATION

- Ph.D. (Chemical Engineering) from Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Saudi Arabia in 2015.
- M.Sc. (Chemical Engineering) from Department of Chemical Engineering, University of Engineering & Technology, Peshawar, Pakistan in 2011.
- B.Sc. (Chemical Engineering) from Department of Chemical Engineering, University of Engineering & Technology, Peshawar, Pakistan in 2007.

RESEARCH INTERESTS

Water treatment, Carbon based membranes, Nano-materials, Adsorption, Biofuels.

TEACHING AND RESEARCH

Lecturer-B Sep 2012 to date
Department of Chemical Engineering
King Fahd University of Petroleum and Minerals (KFUPM)
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Courses taught to B.Sc. (Chemical Engineering) students: Chemical Engineering Labortory-1 (Fluid Mechanics, Heat Transfer & Mass Transfer)

Lecturer June 2007 to May 2012
Department of Chemical Engineering
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Courses taught to B.Sc. (Chemical Engineering) students: Chemical Reaction Engineering, Fluid Mechanics, Introduction to Chemical Engineering-I, Chemical Engineering Mathematics, Particle Technology.

Semester Coordinator May 2010 to June 2011
Department of Chemical Engineering
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Visiting Lecturer Oct 2010 to May 2012
Abasyn University
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Courses taught to B.Tech. Students: Chemical Reaction Engineering, Fuel & Combustion, Heat Transfer.

INDUSTRIAL EXPERIENCE

- Four weeks internship in Pakistan Refinery Limited, Karachi (Pakistan) in 2005.
- 45 days internship in Dawood Hercules Chemicals Limited, Lahore, Pakistan (Worked on Urea Synthesis Unit) in 2006.

WORKSHOPS AND SEMINARS

- Got a certificate in workshop on "Teaching methodologies" arranged by Higher Education Commission (HEC) of Pakistan in July 2007.
- Got a certificate in workshop on "Communication skills and Micro-teaching" arranged by Higher Education Commission (HEC) of Pakistan in 2011.

HONORS AND AWARDS

- **Gold Medal** for First Position in B.Sc Chemical Engineering May 2007
- Open Merit Scholarship for **PhD** Study from KFUPM to Mar 2015 Sep 2012
- Nominated for the Presidential award "**Izaz-e-Fazilat**" by Higher Education Commission (HEC) of Pakistan. Sep 2007
- Winner of the **MEPEC 2015 ChemME** debate competition in Bahrain Sep 2015

MEMBERSHIP

- Member of the Pakistan Engineering Council (PEC).
- Member of the American Institute of Chemical Engineers, Saudi Arabian Section (SAS-AIChE).
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LANGUAGES

English (Fluent), Urdu (Fluent), Pashto (Fluent), Arabic (Basic)

US PATENT

- Muataz Ali Atieh, **Ihsanullah,** Tahar Laoui, Fabrication of carbon nanotube membranes, U.S. Patent Application 14919331, filed October 2015. Patent Pending.

JOURNAL PUBLICATIONS

1. **Ihsanullah,** A.M. Al-Amer, Tahar Laoui, Aamir Abbas, Nasser Al-Aqeeli, Faheemuddin Patel, Marwan Khraisheh, Muataz Ali Atieh, Nidal Hilal. "**Fabrication and antifouling behaviour of a carbon nanotube membrane**". Materials and Design 89 (2016) 549-558.

2. **Ihsanullah,** Tahar Laoui, A.M. Al-Amer, Amjad B. Khalil, Aamir Abbas, Marwan Khraisheh, Muataz Ali Atieh. "**Novel anti-microbial membrane for desalination pretreatment: A silver nanoparticle-doped carbon nanotube membrane**". Desalination 376 (2015) 82-93.

3. **Ihsanullah,** A. Abbas, A. M. Al-Amer, T. Laoui, M. Almarri, M. Khraisheh, M. A. Atieh, M.S. Nasser. "**Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications**". Separation and Purification Technology 157 (2016) 141-161.

4. **Ihsanullah,** Fahad Abdulaziz Al-Khaldi, Basil Abusharkh, Mazen Khaled, Muataz Ali Atieh, M.S. Nasser, Tahar Laoui, Shilpi Agarwal, Inderjeet Tyagi, Vinod Kumar Gupta. "**Adsorptive removal of cadmium (II) ions from liquid phase using acid modified carbon-based adsorbents**". Journal of Molecular Liquids 204 (2015) 255-263.

5. **Ihsanullah,** Hamza A. Asmaly, Tawfik A. Saleh, Tahar Laoui, Vinod Kumar Gupta, Muataz Ali Atieh. "**Enhanced adsorption of phenols from liquids by aluminum oxide/carbon nanotubes: Comprehensive study from synthesis to surface properties**". Journal of Molecular Liquids 206 (2015) 176-182.

6. **Ihsanullah,** Fahad Abdulaziz Al-Khaldi, Basel Abu-Sharkh, Abdalla Mahmoud Abulkibash, M. Imran Qureshi, Tahar Laoui, Muataz Ali Atieh. "**Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes**". Desalination and water treatment 57 (2016) 7232-7244.

7. **Ihsanullah,** Sumaira Shah, Muhammad Ayaz, Iftikhar Ahmad, Murad Ali, Naveed Ahmad, Irshad Ahmad. "**Production of biodiesel from algae**". Journal of Pure and Applied Microbiology 9(1) (2015) 79-85.

8. Hamza A. Asmaly, **Ihsanullah,** Basim Abussaud, Tawfik A Saleh, Tahar Laoui, Vinod Kumar Gupta, Muataz Ali Atieh. "**Adsorption of phenol by aluminum oxide impregnated fly ash**". Desalination and water treatment 57 (2015) 6801-6808.

9. Naveed Ahmad, Farooq Ahmad, **Ihsanullah,** Adnan Daud Khan. "**Studies on the oxidative removal of sodium thiosulfate from aqueous solution**". Arabian Journal of Science and Engineering 40(2) (2015) 289-293.

10. Hamza A. Asmaly, Basim Abussaud, **Ihsanullah,** Tawfik A. Saleh, Vinod Kumar Gupta, Muataz Ali Atieh. "**Ferric oxide nanoparticles decorated carbon nanotubes and carbon nanofibers: from synthesis to enhanced removal of phenol**". Journal of Saudi Chemical Society 19 (2015) 511-520.

11. Basim Abussaud, Hamza A. Asmaly, **Ihsanullah,** Tawfik A. Saleh, Vinod Kumar Gupta, Muataz Ali Atieh. "**Sorption of phenol from waters on activated carbon impregnated with iron oxide, aluminum oxide and titanium oxide**". Journal of Molecular Liquids 213 (2016) 351-359.

12. Hamza A Asmaly, Basim Abussaud, **Ihsanullah,** Tawfik A. Saleh, Alaadin A. Bukhari, Tahar Laoui, Ahsan M. Shemsi, Vinod K. Gupta, Muataz Ali Atieh. "**Evaluation of micro and nano carbon-based adsorbents for the removal of phenol from aqueous solutions**". Toxicological & Environmental Chemistry 97(2015) 1164-1179.

13. Aamir Abbas, Basim Abussaud, **Ihsanullah,** Nadhir Al-Baghli, Marwan Khraisheh, Muataz Ali Atieh. "**Benzene removal by iron oxide nanoparticle decorated carbon nanotubes**". Journal of Nanomaterials (2015), Article ID 587958 .

14. **Ihsanullah,** Muhammad Imran Ahmad, Mohammad Younas. "**Optimization of saponification reaction in a continuous stirred tank reactor (CSTR) using design of experiments"**. Pakistan Journal of Engineering and Applied Sciences 16 (2015) 84-92.

15. Sikandar Khan, Kamran Shah, Izhar-Ul-Haq, Hamid Khan, Sajid Ali, Naveed Ahmad, Muhammad Abid, Haider Ali, **Ihsanullah,** Mazhar Sher. "**Observation of the starting and low speed behavior of small horizontal axis wind turbine**". Journal of Wind Energy (2014), Article ID 527198. http://dx.doi.org/10.1155/2014/527198

CONFERENCE PAPERS

1. **MEPEC 2015**, Conference, Kingdom of Bahrain 2015 Sep 2015
   Poster presentation "Carbon nanotubes membranes: A new frontier in water treatment technology".

2. **Recent Development in Advanced Membranes and Porous Materials for Energy, Environment and Water Applications**
   KAUST, Saudi Arabia 2015 Feb 2015
   Poster presentation "Synthesis and characterization of silver doped carbon nanotubes membrane using a novel technique".

3. **NANO 2014 Conference,** Lomonosov Moscow State University, Russia 2014 July 2014
   Poster presentation "Comparative study of the removal of cadmium (II) from water by using regular and modified Carbon Nanofibers".

4. **The Second Middle East Process Engineering Conference & Exhibition (MEPEC 2013)**
   Kingdom of Bahrain 2013 Oct 2013
   Oral presentation "Effect of MWCNTs on grafted polymer (HDPE-MA)/CNT composite properties".